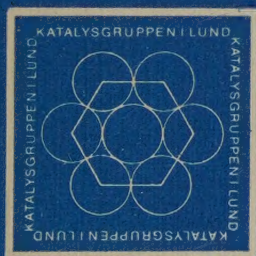


STUDIES ON SOME COORDINATION CATALYSTS  
OF PALLADIUM AND RHODIUM  
with special emphasis on their use  
as catalysts for the hydrogenation  
of fatty oils



CARLAXEL ANDERSSON

Lund 1981







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STUDIES ON SOME COORDINATION CATALYSTS OF  
PALLADIUM AND RHODIUM

WITH SPECIAL EMPHASIS ON THEIR USE AS CATALYSTS  
FOR THE HYDROGENATION OF FATTY OILS

CARLAXEL ANDERSSON

LUND 1981



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|                                                                                                                                                                           | Abstract<br><p>The formation of <math>\text{Pd}^{2+}</math> complexes in phosphinated crosslinked polystyrene resins (P-PS) and the <u>catalytic properties</u> of such compounds in the hydrogenation of soybean oil have been studied.</p> <p>By the use of <u>IR-spectroscopy</u> and <u>analytical techniques</u> it has been shown that <u>ligand displacement reactions</u> starting from (i) <u>bis-pyridinepalladium(II)chloride</u> result in the formation of two different <math>\text{Pd}^{2+}</math> complexes in the resin viz. the <u>monosubstituted complex</u> <math>\text{Cl}_2\text{Pd}(\text{pyridine})(\text{P-PS})</math> and the <u>disubstituted complex</u> <math>\text{Cl}_2\text{Pd}(\text{P-PS})_2</math>, and starting from (ii) <u>bis-benzonitrilepalladium(II)chloride</u> result in the formation of the disubstituted complex <math>\text{Cl}_2\text{Pd}(\text{P-PS})_2</math> together with complexes of the type <math>(\text{PS-P})-(\text{PdCl}_2)_n-(\text{P-PS})</math>, where <math>n &gt; 2</math>, with <u>bridging chlorine atoms</u>.</p> <p>The relative proportion of the constituents in the resin depends on (i) polymer properties such as BET-surface area and content of phosphine groups, (ii) metal loading of the polymer.</p> <p>A method to calculate the amount of <u>inaccessible phosphine groups</u> in the polymer has been presented.</p> <p>Hydrogenation experiments have shown that the catalysts can be used under ambient conditions, with a high <u>polyene selectivity</u> but with the formation of high levels of <u>trans-isomers</u>. A temperature dependent activation of the catalysts has been observed.</p> <p>XPS and X-ray diffraction measurements and a <u>chemical redox method</u> have been used to elucidate the nature of the species in the activated catalyst. It has been shown that the activated catalyst contains two types of palladium species viz. <u>palladium metal</u> and <u>palladium(II) phosphine complexes</u>.</p> <p>Cationic rhodium(I) phosphine complexes have been studied as catalysts for the hydrogenation of soybean oil. These catalysts give a good yield of products with <u>cis-configuration</u>. With the ligand 1,2-bis-(diphenylphosphino)ethane high activity under mild conditions (1 atm <math>\text{H}_2</math>, <math>30^\circ\text{C}</math>) has been found. The results are interpreted on the basis of a <u>monohydride - dihydride equilibrium</u>.</p> |       |
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STUDIES ON SOME COORDINATION CATALYSTS OF PALLADIUM AND RHODIUM  
with special emphasis on their use as catalysts for the hydro-  
genation of fatty oils.

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The thesis consists of this summary and the following papers,  
referred to in the text by their Roman numerals:

- I. Hydrogenation of Fatty Oils Under Mild Conditions with  
Palladium-based Coordination Catalyst Anchored to  
Organic Polymer Matrices  
C. Andersson and R. Larsson  
Chemica Scripta 15, 1980, 45
- II. Investigations on the Conditions for Hydrogenation of  
Fatty Oils with Polymer Anchored Pd-phosphine Complexes  
C. Andersson and R. Larsson  
Accepted for publication in J. Am. Oil Chem. Soc.
- III. Synthetic and Infrared studies on Polymer Bound  
Palladium Phosphine Complexes  
C. Andersson and R. Larsson  
Submitted for publication in J. Catalysis
- IV. Active Sites in Polymer-Bound Palladium - Phosphine  
Coordination Catalysts. Chemical and XPS investigations  
C. Andersson and R. Larsson  
Submitted for publication in J. Catalysis
- V. Catalytic Hydrogenation of Soybean Oil with Rh(I)  
Dihydride Complexes as Catalysts  
C. Andersson and R. Larsson  
J. Am. Oil Chem. Soc. 58, 1981, 54



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## A. INTRODUCTION

## A 1. CATALYTICAL HYDROGENATION OF FATTY OILS

Some historical remarks

In the beginning of this century Sabatier (1) showed that the action of finely divided nickel metal makes it possible to combine molecular  $H_2$  and gaseous olefins to the corresponding saturated hydrocarbon. This discovery was soon utilized by Normann (2) who invented the so called catalytical hydrogenation of fatty oils. By the addition of hydrogen to the unsaturated bonds in the fatty oil an increase in melting point was achieved, i.e. liquid fats could be converted to fats that were solid at room temperature.

The production of margarine depends critically on the supply of solid fats. The invention of catalytical hydrogenation expanded the base of raw materials for the margarine production, since by this procedure also fats that are liquid at room temperature could be used in the production of margarine.

Also one other factor contributed to the importance of this process. An increased resistance of the fats against oxidative deterioration was observed for fats subjected to catalytic hydrogenation. Thus fats that previously had been inedible, could be converted and used for human consumption.

Modern aspects

Today reasons for performing catalytic hydrogenations of fatty oils are basically the same as those at the time of invention, viz., to increase the melting point and/or to reduce the oxidative breakdown of the fats. However, besides these primary reasons, certain other aspects on the hydrogenation process can be stated.

Technical aspects

These are largely connected to developments in the industrialized society as such. Increased standard of living, with



improved communications and trade, has increased the consumers demand for fats of high and uniform quality. Independent of the variations in raw materials supply, that occurs owing to annual variations in the crop, the consumers demand a uniform product. The number of different fat products has also increased with increased standard of living. Products specified for certain uses e.g. frying margarine, soft margarines for refrigerated storage, salad oil and so on are nowadays manufactured. To meet the requirements on these new products one needs a technique of modification that enables the production of fats with narrowly specified melting characteristics and texture properties.

#### Nutritional aspects

Progress in medical and biochemical sciences have clearly shown that dietary fats do not only supply energy but that they play a specific metabolic role. This is perhaps best exemplified with the so called essential fatty acids (3). They are unsaturated fatty acids with specific double bond structure which has been found essential for maintaining animals and man in a healthy condition. The most important of these acids is linoleic acid.

Yet another effect of dietary fatty acids frequently discussed during the last two decades is the role of saturated acids in the genesis of heart diseases. It has been claimed that high levels of saturated acids in the diet are undesirable. Finally the recent discussion on the effect of trans-acids in human diet (4) must be recognized.

Thus from the nutritional point of view certain limitations on the catalytic process has developed: The hydrogenation should not result in the formation of completely saturated acids. The formation of trans and other isomeric acids should be low. A certain level of essential fatty acids must be retained.

### Some general features of the hydrogenation process

Modern analytical techniques have shown that hydrogenated fats are in fact very complex mixtures of isomeric fatty acids (5). This means that the rather simple reaction discovered by Sabatier, viz., the addition of dihydrogen to the double bond in the olefin, is not the only reaction that takes place. The catalyst does also promote different isomerisation reactions, e.g. the formation of positional and geometric (cis-trans) isomers. The extent of these side reactions depends strongly on reaction conditions such as temperature, pressure, catalyst concentration, agitating speed (6) and also on the type of catalyst used (7).

Furthermore, various catalysts can differ in activity towards different types of fatty acids. E.g. one can find for a certain catalyst a preference for the triene fraction of the fat mixture over the diene one. Such a catalyst is said to show a high triene selectivity. In the same way diene and monoene selectivity can be qualitatively defined.

The catalysts characteristics, such as isomerisation tendency and selectivities, influence the quality of the hydrogenated oil in various ways. E.g., Ni catalysts used in industry today, can hydrogenate fats to a high technical quality i.e. good melting and texture properties. However, the linolenate selectivity for the Ni catalyst is rather low. Consequently in order to increase the oxidative stability of an oil (decrease the linolenate content), a large portion of the linoleate of the oil has to be sacrificed. In addition considerable amounts of trans-acids are formed. The formation of trans-acids and the reduction of linoleate content is, from a nutritional point of view, not desirable. On the other hand if the reaction conditions are changed to reach a better linolenate selectivity an even larger amount of trans-isomers are formed (8).

It is thus difficult, to fulfill both the technical and the nutritional demands on the hydrogenation process with the existing catalyst. This difficulty motivates the search for new types of catalysts.



## A 2. COORDINATION COMPOUNDS AS CATALYSTS FOR THE HYDROGENATION OF FATTY OILS

Two main lines can be traced in the literature concerning the search for new types of catalysts. One originates from the high triene selectivity found for heterogeneous copper catalysts (9, 10), the other originates from progress in the organometallic chemistry of the transition metals during the last decades. The introduction in 1962 of soluble coordination compounds as catalysts for the hydrogenation of fatty oils (17) was a new approach to the selective hydrogenation of linolenate. Several different systems were also studied. The Northern Regional Center performed studies on pentacyanocobaltate, metalcarbonyls (Fe, Co, Mn, Cr, Mo, W) and metalacetylacetonates (Ni, Co, Fe, Cu) (11). Yet another type of system studied at that time was triphenylphosphine complexes of Ni, Pd or Pt (12, 13, 14, 15, 16).

The reasons for introducing this new type of catalysts can be found in the following quotation (17), "In 1962 we initiated a new approach to the study of selective hydrogenation by using soluble organometallic compounds as catalysts. Practically, we wanted to know if greater selectivity would be possible with homogeneous metal catalysts. Basically, we wished to gain a better understanding of the mechanism of fat hydrogenation."

Much basic knowledge of the hydrogenation process has also been collected since the study of metal coordination compounds as catalysts was started in the early sixties. Just to mention a few important results one can point to the isolation of possible reaction intermediates e.g. the isolation of complexes with conjugated dienes  $\pi$ -bonded to  $\text{Fe}(\text{CO})_3$ , and the isolation of hydridocomplexes of Pt by reaction of the catalyst  $\text{Cl}_2\text{Pt}(\text{PPh}_3)_2 - \text{SnCl}_2$  with molecular hydrogen (13).

Also kinetic measurements with these catalysts have provided much mechanistic information on the hydrogenation process.

The essential features of some of the catalysts that have been studied, have been reviewed by Frankel and Dutton (11)

and more recently by Frankel (17).

It follows that one of the aims given in the quotation above, viz., to reach a better understanding of the mechanism of hydrogenation, can be said to have been reached. However, none of the systems studied, have found industrial application, although some of them give products that are in better correspondence with the demands stated in the introduction than the products are that have been obtained with traditional Ni catalysts.

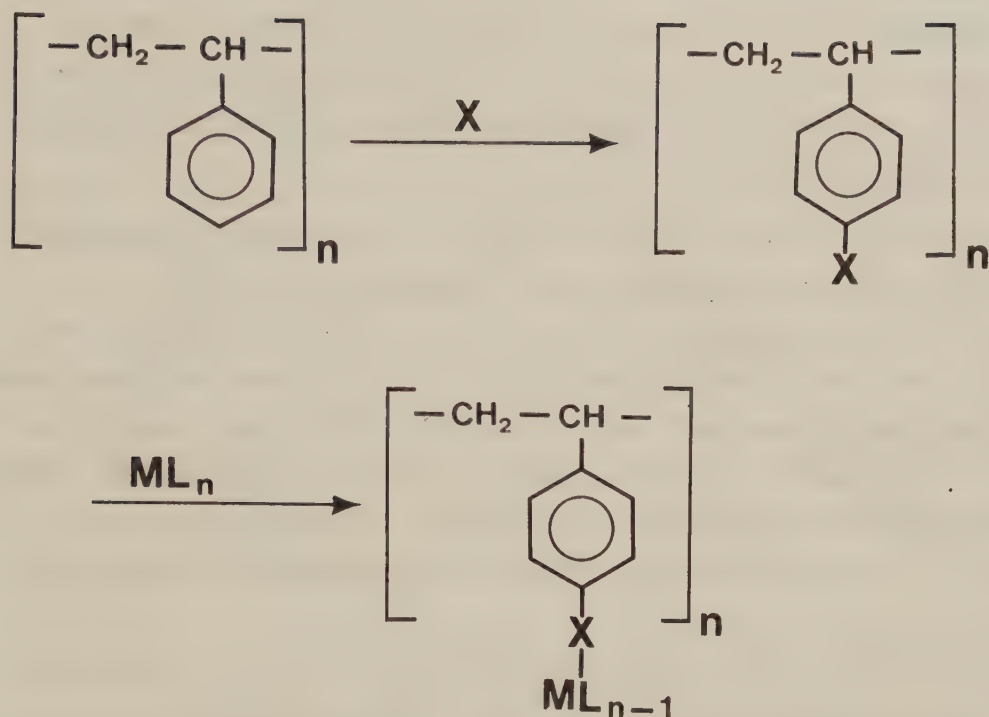
The prime factor which have limited the industrial use of these catalyst systems is the problem of catalyst separation and reuse. From a nutritional as well as from an economic point of view the complete removal of these soluble metal complexes from the oils is necessary.

### A 3. THE IMMOBILISATION OF SOLUBLE COORDINATION CATALYSTS

One rather obvious way to overcome the problem of catalyst recovery is to make the catalyst insoluble, and thus enable the separation to be done by simple filtration. The first - to my knowledge - published idea in this direction concerning complexes previously used to hydrogenate fatty acids can be found in a paper by Bailar (18). In this paper, published 1970, a rather brief description of polymeric nonchelating phosphine ligands, intended to be used in heterogeneous platinum catalysts, can be found. The use of different kinds of such polymeric ligands to immobilize homogeneous coordination catalysts soon became an active field of research (19).

The technique, most frequently used to prepare such polymer linked complexes, is to functionalize crosslinked polystyrene resins and then to react this polymer with a suitable metal salt or metal complex. Very schematically this procedure can be described in the following way





where X is a functional group such as amine, phosphine.

Using this technique, i.e. treating a chloromethylated Amberlite XAD-4 resin with  $\text{LiPPh}_2$  to introduce phosphine groups in the polymer and then reacting this with the complex  $\text{X}_2\text{ML}_2$  (X = halogen, L = benzonitrile and M = Pd or Pt), Bruner (20, 21, 22) prepared heterogeneous analogues of the homogeneous complexes previously investigated as catalysts for the hydrogenation of soybean oil methylester (12 - 16). These heterogeneous catalysts were used to hydrogenate various substrates, among which also soybean oil methylester. These hydrogenation studies showed that the catalysts were active and that they could be recovered by filtration and reused.

Judging by these early reports this technique seemed as an interesting approach to the important problem of catalyst separation and reuse. As an extension of previous work on homogeneous catalysis and fat hydrogenation we found it interesting to study this "new" technique of catalyst immobilisation.

#### A 4. THE AIM OF THE PRESENT STUDY

Very generally described the present study has been directed towards the search for a catalyst that enables the hydrogenation to be done according to the demands described in the introduction.

A more specific objective has been to study heterogenized metal coordination compounds and their applicability as catalysts for the hydrogenation of fatty oils. During the course of this work it became obvious that a better knowledge of the complex formation in polymeric resins was highly desirable. Consequently great efforts has been made to increase the knowledge of the system we choose to investigate. The results of this part of the study are reported in papers I - IV.

Recent interest in the nutritional aspects of trans-fatty acids (4) has emphasized the need for catalysts giving low trans content in the resulting oil. Therefore we focused our attention on systems yielding high cis/trans ratios. The results obtained so far, with this specific aim, are presented in paper V. For the sake of clarity, I will in the following treat the heterogenized catalysts and the systems intended for high cis/trans ratios separately although no sharp boarderline between the two exists. Once a homogeneous catalyst with good trans-characteristics is found, it has to be heterogenized, one way or the other, to be technically applicable.

#### B. HETEROGENIZED METAL COORDINATION CATALYSTS

##### B 1. THE CHOICE OF CATALYST SYSTEM

One important criterion, in the selection of a suitable system to study in the heterogenized state is, that the essential properties of the homogeneous analogue are known. In that way a comparison can be made and the effects of the heterogenization can be studied.

Among those systems previously studied in solution (11, 17), the phosphine complexes of Ni, Pd and Pt were considered most



interesting since they have a high polyene selectivity. In addition these systems had been shown to be possible to heterogenize (20,21,22) via phosphine groups incorporated in a polymeric resin.

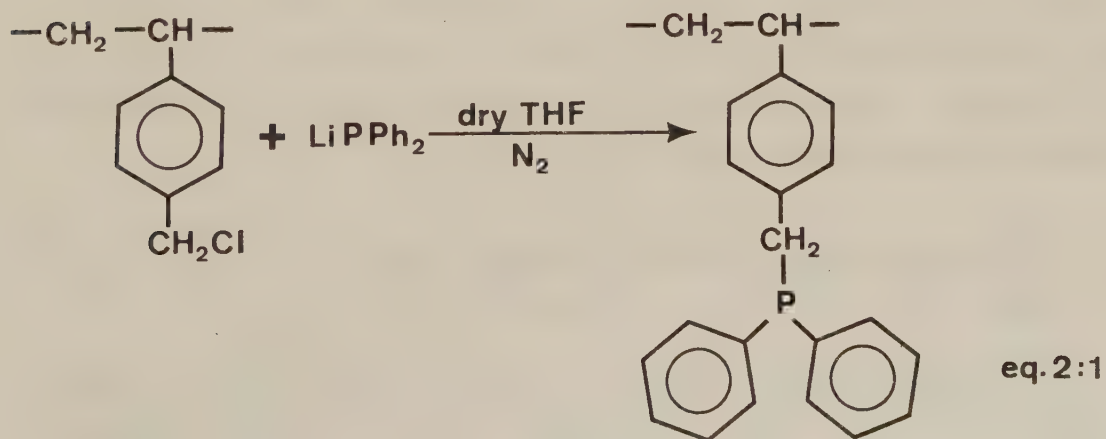
The other homogeneous systems e.g. the arene  $\text{Cr}(\text{CO})_3$  complexes with interesting selectivity characteristics have no ligand that can be utilized in the bonding to a polymeric resin. The arene ligand in this catalyst probably functions as a leaving group in the rate determining step (23) and hence a possibility for metal leakage from the carrier exists if the arene ligand had been utilized for anchoring purposes. Such a leakage has also been noted (24). Consequently the arene  $\text{Cr}(\text{CO})_3$  type of complexes can not be heterogenized with the technique that are known today.

The chief disadvantage of the phosphine complexes of Ni, Pd and Pt is that they promote the formation of high levels of trans-acids. At the time this project was started this was, however, not considered as a serious drawback, and Pd-phosphine complex was chosen.

## B 2. PREPARATION OF THE CATALYSTS

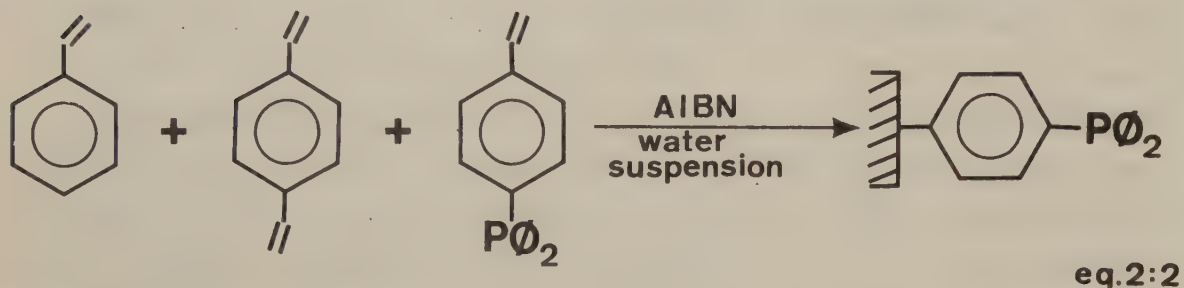
### Preparation of resins

Starting from commercial chloromethylated crosslinked polystyrene resins the phosphine groups were introduced by the following procedure:



THF = Tetrahydrofuran

Another method that has been used to prepare a phosphinated resin is the copolymerisation of monomers according to the following scheme:

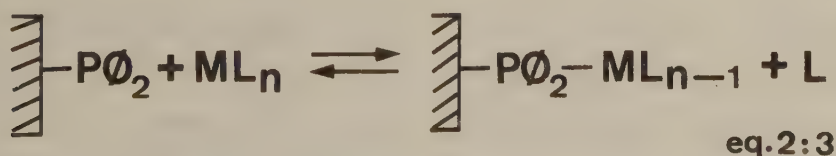


AIBN = azo – isobutyronitrile

A difference exists between these two modes of preparation. In the first one a benzyldiphenylphosphine and in the latter one a triphenylphosphine group is formed. Bailar (18) has found that for homogeneous Pt catalysts the catalytic activity depends on the type of phosphine group coordinated to the metal ( $P(CH_3)_2Ph > P(CH_3)Ph_2 > PPh_3$ ). No evidence for such an effect has, however, been found for the two types of polymers investigated in this study. Accepting the results in this study (IV), that it is Pd metal that makes the heterogeneous catalyst active no such effect should, however, be expected.

#### Preparation of supported metal complexes

Hartley and Vezey (19) have classified and described various methods that can be used to introduce the metal onto the support. The method most frequently applied is based on ligand displacement reactions as follows:



If this method shall succeed, the equilibrium above must be displaced to the right. The equilibrium position depends, however, in its turn on the complexbinding ability of the ligand L relative that of the resinbound ligand. This means

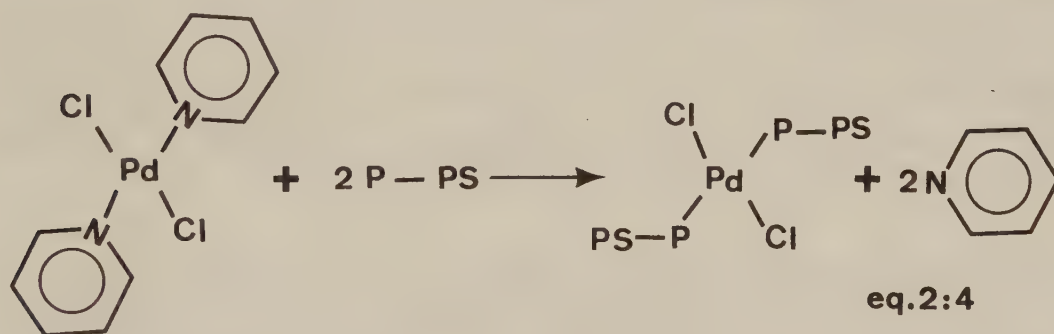


that by the use of a ligand L, which forms only weak complexes with the metal ion M, a favourable equilibrium position can be attained.

This principle was applied by Bruner and Bailar (20,21, 22) in their preparation of Pt and Pd complexes bound to phosphinated polystyrene resins. They used, e.g., Pt and Pd complexes with benzonitrile as ligand in the starting material.

Also in the present study the same procedure has been used in the preparation of catalysts and full descriptions of the preparation procedure can be found in papers I, II and III.

For the first catalyst prepared and studied in the present work a slightly different approach was used, however. Instead of using the complex bis(benzonitrile) $\text{PdCl}_2$  as the starting material the bipyridine complex was used according to the following equation, where P-PS = polymeric phosphine.



In paper I such a preparation is described. Judging from the course of the synthesis nothing indicated that the ligand displacement reaction did not proceed as expected, i.e. that both the pyridine ligands were substituted by phosphine ligands in the polymer. At the time when the experiments were planned the generally accepted view on the mobility of the phosphine groups inside low crosslinked polystyrene resins was that the polymer chain is sufficiently mobile to bring also nonadjacent ligands together (25). We found that

a stochiometric quantity of Pd could be incorporated in the polymer, but no effort was made to analyse the amount of pyridine released by the reaction.

In the hydrogenation experiments performed with this catalyst it was, however, shown (I) that this catalyst behaved differently from its homogeneous analogue in many respects. In the following table (from II) a comparison of the polymeric catalyst and its homogeneous analogue is displayed.

|                                                    | Differences in catalytic behavior        |                                                          |
|----------------------------------------------------|------------------------------------------|----------------------------------------------------------|
|                                                    | $\text{Cl}_2\text{Pd}(\text{P}\phi_3)_2$ | $\text{Cl}_2\text{Pd}$ bound to phosphinated polystyrene |
| Hydrogen pressure necessary for activity           | 35 atm                                   | 1 atm                                                    |
| Induction period                                   | none                                     | yes, depending on temperature                            |
| Colour change during hydrogenation                 | remains yellow                           | changes from light yellow to grey-green                  |
| Effect of co-catalyst addition ( $\text{SnCl}_2$ ) | essential for activity                   | makes the catalyst inactive (1 atm $\text{H}_2$ )        |
| Effect of $\text{P}\phi_3$ addition                | (no reports found)                       | makes the catalyst inactive (1 atm $\text{H}_2$ )        |

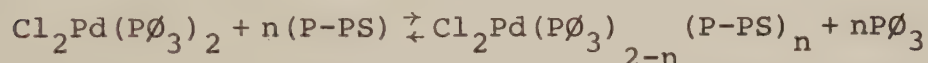
From these observations a model of the polymeric catalyst was suggested, in which other species than the bisphosphine complex were taken into account. As this model was based solely on these hydrogenation experiments, however, it was used in the following only as a working hypothesis, which further experiments could confirm or turn down.

The suggested model implies that the substitution does not proceed solely as described in eq 2:4, but that some easily reduced species are also formed. To try to understand the nature of these species and how the polymer may influence their properties a series of experiments have been performed.

The first step in this testing of the model is reported in II. In this paper the same preparative route as that in I was studied, but this time the pyridine release was determined. The analysis showed that less than two pyridine molecules were released per Pd atom incorporated in the resin.

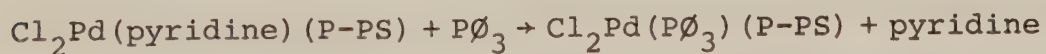
Based on the analytical results as well as infrared studies of the prepared catalyst it was shown that the resin contained two different species. In addition to the expected bisphosphine complex  $\text{Cl}_2\text{Pd}(\text{P-PS})_2$ , also the halfsubstituted complex  $\text{Cl}_2\text{Pd}(\text{pyridine})(\text{P-PS})$  existed, indeed, as the major component.

Paper II also describes two ways to avoid the formation of the halfsubstituted complex. In the first one the substitution reaction was carried out using  $\text{Cl}_2\text{Pd}(\text{P}\emptyset_3)_2$  as the reacting complex according to the following formula:



The equilibrium position for such a preparative route is, however, not favourable since only a small quantity of Pd could be incorporated in this way. This method was used only because the species formed in the resin by this reaction will be bisphosphine complexes, either the complex  $\text{Cl}_2\text{Pd}(\text{P-PS})_2$  or the complex  $\text{Cl}_2\text{PdP}\emptyset_3(\text{P-PS})$  or a mixture of these.

The second method applied to prepare a resin containing only bisphosphine complexes is based on the substitution of the pyridine ligand in the species  $\text{Cl}_2\text{Pd}(\text{pyridine})(\text{P-PS})$  with a monomeric phosphine ligand according to the following:



In paper III which mainly deals with the complex formation in the polymeric resins yet another preparative methods has been used. This method is exactly the same as that used by Bruner and Bailar (20,21,23) namely the substitution of the benzonitrile ligand in  $\text{Cl}_2\text{Pd}(\text{benzonitrile})_2$  by the polymeric phosphine P-PS.



Benzonitrile differs from pyridine in that it is a much weaker complexing agent. This means that in the case of benzonitrile a more favourable equilibrium position can be expected. Judged from the work of Bruner and Bailar (20, 21,22) this seemed to be the case. No indications of species other than the bisphosphine were found in their study. However, comparing the results obtained in our study (paper I, II) with those of Bruner and Bailar it seems highly plausible that even in the benzonitrile case other Pd species than the bisphosphine complex are formed in the resin.

In a study by Pittman et.al. (26) a catalyst with a ratio  $P/Pd=1$  was prepared via the benzonitrile route. Such a phosphine-palladium ratio indicates, however, that species other than a bisphosphine complex must have been formed in the resin.

In those catalysts that we prepared by the pyridine route the existence of the mixed pyridine-phosphine complex could be proved by determining the amount of pyridine released by the reaction. When the same type of analysis were performed in the benzonitrile case, however, the results showed a release of two mole benzonitrile per mole of Pd incorporated.

Consequently no mixed benzonitrile-phosphine complexes analogous to those found for pyridine could have been formed in the resin.

To elucidate the nature of the species formed in the resin when the benzonitrile complex is used as starting material a somewhat different approach has been used. This will be discussed in part B:4.

### B 3. HYDROGENATION EXPERIMENTS

In the motivation given earlier for the choice of catalyst system used in this study it was argued that the properties of the homogeneous analogue are well known. It was also stated that in this way a comparison of the homogeneous and the heterogeneous system can be made.

The results of the hydrogenation experiments performed in this study are given in I-II. In these results no

appreciable differences to those obtained with similar homogeneous systems, can be found. The catalyst prepared and tested in I shows high polyene selectivity just as similar homogeneous systems do (27). Also the formation of trans fatty acids follows the pattern of its homogeneous analogue i.e. high levels of trans acids are formed (II). A more detailed comparison between the two studies can not be meaningful as we used (I and II) the soybean oil without a solvent and Bailar et.al. (21,22) used methylesters of the oil and methanol or methylenechloride as solvent.

However, with respect to other features than the product obtained, the heterogenized catalyst shows major differences compared to the analogous homogeneous system.

In the hydrogenation experiments reported in paper I two observations are important. First the catalyst changes colour from yellow to grey-green. Second the reaction shows a marked temperature-dependent induction period. Similar differences have also been observed in other studies (20, 22).

It was thus obvious that some kind of changes in the catalyst must have taken place. The question was, however: What are the nature of these changes and why do they take place?

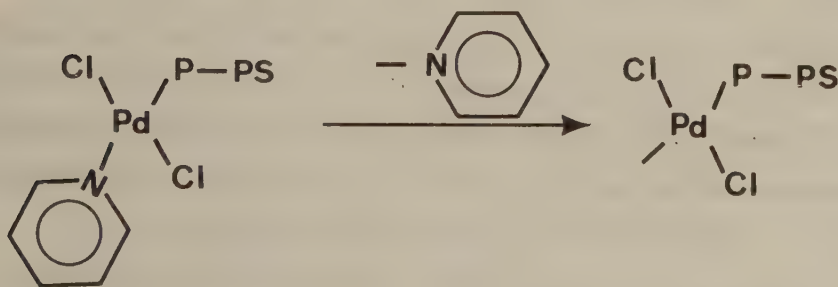
Much of the work in the present study has been devoted to these questions. The reason for this is rather obvious. Firstly in order to modify and change a catalyst to specified uses a detailed knowledge of the active site is necessary. Secondly the conflicting ideas concerning the nature of the activated catalyst that can be found in the literature (20,26,33) necessitate further investigations.

The first attempt to answer this question can be found in I. In that study it was suggested that it is the formation of Pd metal that causes the colourchange of the catalyst. In order to find evidence for metal catalysis the hydrogenation characteristics of the polymer-bound catalyst was compared with that of a commercial Pd on carbon catalyst under identical conditions. The results of this study was that the Pd on carbon catalyst gives the same rate of reaction down to an iodine value of 30, while the reaction rate

for the polymer-bound catalyst decreases when an iodine value in the region of 100 is reached. Hence the Pd/C catalyst does not show the selectivity shown by the polymer-bound palladium catalyst. Since the support as well as the nature of the active site can influence the selectivity of the catalyst this study gave no clear answer to the question whether it is Pd-metal that is formed in the resin on the activation.

As discussed earlier (p. 12) the synthesis of the catalysts described in II, was based on the model suggested in I. According to this model, the catalyst containing the species  $\text{Cl}_2\text{Pd}(\text{pyridine})(\text{P-PS})$  (catalyst 1) should be active, while the other two (catalyst 2 and 3) containing only bisphosphine complexes should be inactive. This was also found in the hydrogenation experiments reported in II. Hence this study showed that the existence of species other than bisphosphine complexes in the resin is essential for catalytic activity under ambient condition.

One other important result, relating to the activation of the catalyst, has been found in the hydrogenation experiments (II). In this study it was shown that the activation is related to a release of pyridine from the catalyst. Hence the metal complex in the resin undergoes changes during the activation.



The further fate of these coordinatively unsaturated complexes can not, however, be discovered through hydrogenation experiments.



#### B 4. INVESTIGATIONS OF THE CATALYSTS

In general, spectroscopic methods are the most powerful means by which structural information on a molecular level can be obtained for not ordered systems. In the study of supported metal complexes, however, the very low concentration of the complex on the support makes most of these methods somewhat limited in use. In addition, because of the low transparency of many supports, optical methods are often difficult to use.

In a review paper by Michalska and Webster (28) treating supported homogeneous catalysts the following quotation concerning these problems can be found:

"Detailed information about the structure of complexes with polymeric ligands is difficult to obtain. Indeed it is our belief that advancement in this area of chemistry could be seriously impeded by this very difficulty."

In the present study much effort has also been made to find methods and techniques by which such information can be obtained.

The main part of these investigations and the experimental details are reported in III and IV but some additional comments might be of interest.

The direct observation of bands which can be assigned to metal-ligand vibrations or internal ligand vibrations can in favourable cases be done by infrared spectroscopy (25). An example of this can be found in II where the existence of the species  $\text{Cl}_2\text{Pd}(\text{pyridine})(\text{P-PS})$  in the resin was confirmed by infrared studies. A band at  $1220\text{ cm}^{-1}$  which also appears in the complex  $\text{Cl}_2\text{Pd}(\text{pyridine})\text{P}\phi_3$  was found in the spectrum of the prepared catalyst. Hence the interpretation was made that a similar complex existed in the resin.

The other example in the present study which gave valuable informations about the structure of the species in the resin is the investigation of metal-halide vibrations in III. In these investigations a band at  $340\text{ cm}^{-1}$  was found in the IR spectra. This band has the same position as the stretching vibration of the Pd-Cl bridges in solid  $\text{PdCl}_2$  (29). Hence

the presence of the band at  $340\text{ cm}^{-1}$  in the spectra of the prepared catalysts indicated that the structure of the species in the resin is similar to the structure of  $\text{PdCl}_2$  i.e. chains of chloride-bridged  $\text{PdCl}_4$  units.

In those cases where information is not obtainable by the direct study of the species in the resin an indirect approach can be used. This involves a chemical conversion of the species of interest to one more easily detected by spectroscopic means. Information obtained this way must however be interpreted carefully since chemical reasoning must be used to derive the structure of the species originally present. To design a suitable chemical method to convert the species in the resin, some vague idea of the nature of this species is often necessary. Used with chemical sense this method of combining chemical and spectroscopic techniques can be of great value.

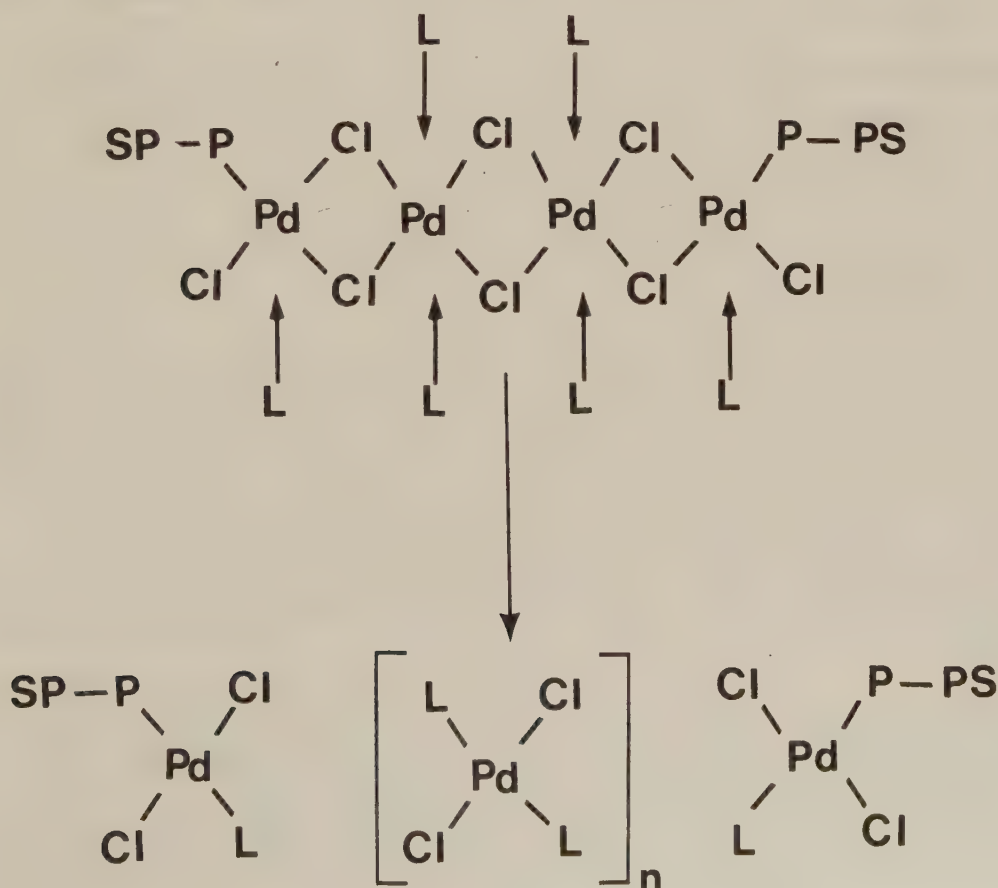
In the present study the method outlined above has been used to study the species formed on reaction of a phosphinated resin with  $\text{Cl}_2\text{Pd}(\text{benzonitrile})_2$  (III). In these resins it was suspected that chloride bridged species were present. Such halide bridged complexes are known to be easily cleaved by Lewis bases, like amines, or carbonmonoxide (30), and hence such reagents have been used in this study. One important criterion in the choice of the Lewis base was that it should have easily detectable IR active bands.

In the present study CO and 4-cyanopyridine have been used for this purpose. In the IR spectrum obtained directly after reaction with CO two peaks were present in the CO stretching region. One band at  $2125\text{ cm}^{-1}$  and another at  $1925\text{ cm}^{-1}$ . On storage of the CO-treated sample in moist air the peak at  $2125\text{ cm}^{-1}$  in the original spectrum disappeared and a new peak at  $1970\text{ cm}^{-1}$  appeared. The peak at  $1925$  was unchanged.

The interpretation made from these observations is that the catalyst contains chloride bridged species of the type  $\text{PS-P}(\text{PdCl}_2)_n\text{-P-PS}$ . On reaction with CO this structure is broken to yield two types of carbonyl complexes viz. one type resulting from CO coordinated to the end units and another type resulting from CO coordinated to the interca-

lated  $\text{PdCl}_2$  units in the chain. The change observed in the spectrum i.e.  $2125 \rightarrow 1970$  is very similar to that observed on reaction of  $\text{PdCl}_4^{2-}$  with CO (44). Hence the peak at  $2125 \text{ cm}^{-1}$  was assigned to the  $\text{PdCl}_2$  units in the chain, while the peak at  $1925 \text{ cm}^{-1}$  was assigned to the end units.

The same type of structure was also indicated on reaction with 4-cyanopyridine. In this case two observations support this interpretation. Firstly in the infrared spectrum a very weak band at  $2239 \text{ cm}^{-1}$  was present. On comparison with the spectrum of the complex  $\text{Cl}_2\text{Pd}(\text{P}\emptyset_3)(4\text{-cyanopyridine})$  this was assigned to the  $\text{C}\equiv\text{N}$  stretch in the species  $\text{Cl}_2\text{Pd}(\text{P-PS})(4\text{-cyanopyridine})$ . Secondly on reaction with 4-cyanopyridine it was observed that quite a large part of the palladium in the resin was extracted out of the polymer as the complex  $\text{Cl}_2\text{Pd}(4\text{-cyanopyridine})_2$ . This observation supports the suggested structure since an attack by the Lewis base on the chloride bridges will result in the formation of such complexes. Taken together the results obtained and the interpretation made on reaction with the Lewis bases can be summarized as follows:





Even elemental analysis data can be of great value in the study of the complexes formed in a polymeric resin. An example from the present study (III) can help to illustrate this statement. In the preparations reported in III P/Pd ratios less than two can be found. Actually also such low ratios were observed by Pittman et al. (26) but not commented upon. Having found such ratios it is obvious that palladium bisphosphine complexes can not be the only Pd complex in the resin.

One problem relating to this example is the accessibility of the phosphine groups inside a polymer network. Grubbs and Sweet (31) have used microprobe analysis to determine the distribution of phosphine groups and metal atoms inside a 2% crosslinked polymer. Using an excess of metal complex in the preparation they found a uniform distribution of metal atoms and phosphine groups throughout the polymer cross section. This finding indicates that the polymer network can be penetrated by the reacting molecules. This does not, however, mean that all phosphine groups are equally accessible in the sense that they can coordinate to a metal atom.

Phosphorous elemental analysis gives the total phosphine concentration in the polymer. In discussions of phosphine/metal ratios the total amount of phosphines in the polymer is, however, not relevant. The interesting thing to know in such discussions is the amount of phosphine accessible for coordination.

This quantity is in general not easily determined. Phosphorous NMR has, however, been used to determine the amount of phosphine complexed and this seems to be a very powerful method in such studies (32). In the present study (III) an attempt has been made to use elemental analysis data to calculate the amount of inaccessible phosphine groups in the polymer.

Assuming that a certain concentration of inaccessible phosphine groups  $C'_P$  exists in the polymer and further that the species  $Cl_2Pd(P-PS)_2$  and  $Cl_2Pd(pyridine)(P-PS)$  are the only Pd complexes in the resin the following relation can be

derived:

$$C_{Pd} = 1/2 (C_P + C_{py} - C'_P)$$

where  $C_{Pd}$  is total palladium concentration

$C_P$  is total phosphine concentration

$C_{py}$  is the concentration of coordinated pyridine

Hence analyzing these quantities for a polymer treated with varying amounts of the complex  $Cl_2Pd(pyridine)_2$  enables the determination of  $C'_P$  (the intercept with the abscissa axis).

In the study reported in paper III this method has been used to determine  $C'_P$  values for three different polystyrene resins.

The results show that the concentration of inaccessible phosphines in the polymers can not be neglected. If the exact value of  $C'_P$  is not known one can aim at too large a factor metal/phosphine in the preparation of the catalyst. Hence undesired complexes might result.

The reason for the inaccessibility of a part of the phosphine groups in the resin have in III been discussed in terms of polymer properties i.e. sterically hindrance of the groups. The polymer with low BET surface area ( $1.5 \text{ m}^2/\text{g}$ ) was found to contain relatively more inaccessible phosphine groups than the polymer with higher area ( $53.5 \text{ m}^2/\text{g}$ ).

Another possible explanation for the effect found, i.e., that only a part of the phosphine groups can be used in metal bonding, is the oxidation of the phosphine groups to phosphine oxide. In the IR spectra of the polymers studied no sign of such oxidation products have, however, been found.

To settle this question better methods to detect phosphine oxide in the polymers must be used. Grubbs and Su (32) have noted that  $P^{31}$  NMR can be used for this purpose and a comparative study using  $P^{31}$  NMR is planned.

The methods discussed so far have been applied to study unused catalysts. Taken together the results of these investigations show that the polymeric resin contains two kinds of species as suggested in the working hypothesis i.e.

$\text{Cl}_2\text{Pd}(\text{P-PS})_2$  and  $\text{Cl}_2\text{Pd}(\text{pyridine})(\text{P-PS})$  in those catalysts which are prepared from  $\text{Cl}_2\text{Pd}(\text{pyridine})_2$  and in those prepared from  $\text{Cl}_2\text{Pd}(\text{benzonitrile})_2$  the species  $\text{Cl}_2\text{Pd}(\text{P-PS})_2$  and  $(\text{P-PS})-(\text{PdCl}_2)_n-(\text{P-PS})$ .

According to the model suggested in I the activation of the catalyst is caused by a reduction of those  $\text{Pd}^{2+}$  ions not coordinated to two phosphine ligands. Some observations made during the hydrogenation experiments i.e. that the catalysts change colour from yellow to grey-green and that they are active under low hydrogen pressure (1 atm) was the basis for this part of the model. However, no decisive conclusion of the nature of the active species in the catalyst can be drawn from such observations.

Therefore, studies of the activated catalyst i.e. the grey-green form, with methods sensitive to the oxidation state of the metal atom in the catalyst, had to be done.

The methods applied in these studies were X-ray photoelectron spectroscopy, X-ray diffraction and a chemical method based on the redox couple benzoquinone/hydroquinone.

X-ray diffraction techniques can be used to identify solid crystalline phases. Hence if palladium metal is formed in the resin on activation it should be possible to detect. Even this method is, however, limited by the low amount of the metal phase in the catalyst.

By this technique the existence of palladium metal could be demonstrated only in the catalyst with the highest metal content, although the same colour change appeared for all the catalysts studied. (2.58% Pd, 3.64% Pd and 6.64% Pd).

As suggested in the model of the activated catalyst even unreduced  $\text{Pd}^{2+}$  complexes is present in the resin. To demonstrate such species other methods have to be used e.g. X-ray photoelectron spectroscopy (XPS, ESCA).

XPS is a spectroscopic technique sensitive to the chemical state of the atom concerned e.g. the binding energy is related to the oxidation state and mode of bonding. Terasawa et.al. (33) found, however, only a small difference in binding energy of Pd between fresh and used catalysts. This



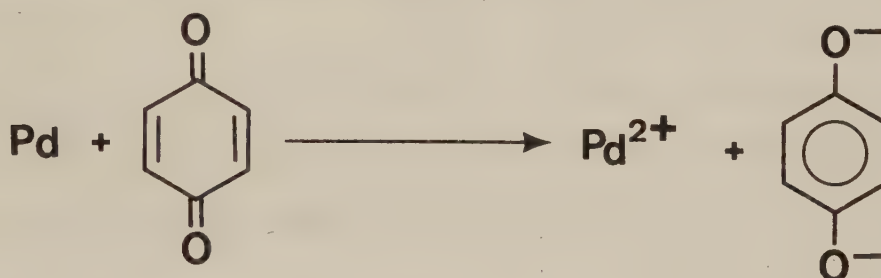
would indicate only a minor change on activation.

For the two catalysts with low metal content (2.58% Pd and 3.64% Pd) a similar observation, i.e. no change in Pd binding energy on activation, was made in the study reported in IV.

For the catalyst with the highest metal content (6.64% Pd), on the other hand, the XPS measurements showed two chemically different Pd species in the activated catalyst. Although electrostatic charging of the insulating polymer and surface oxidation of the metal phase made interpretation a difficult task, it was possible to show the existence of  $\text{Pd}^{2+}$  and Pd metal.

Yet another method has been designed and applied to determine the nature of the activated catalyst and details of this method are reported in IV.

This method is of chemical nature and is based on the oxidation of Pd metal by benzoquinone and the subsequent analysis of the amount of hydroquinone formed.



Hence, from a knowledge of the total amount of Pd in the activated catalyst and the amount of free metallic palladium from the above mentioned method, one can determine the ratio  $\text{Pd}^0/\text{Pd}^{2+}$ .

One question that can be raised concerning this method is the following: Is it certain that Pd metal acts as the electron donor towards benzoquinone, or can it be other reducing agents in the polymer? The answer is no. The method has to be used in conjunction with other methods. This has also been the case in the study reported in IV and some interesting comparisons can be done concerning the results of the three methods used. They are summarized in the table below.

| Pd <sub>tot</sub> (%) | X-ray diffraction | XPS                         | Redox method |                    |
|-----------------------|-------------------|-----------------------------|--------------|--------------------|
|                       |                   |                             | Pd met %     | Pd <sup>2+</sup> % |
| 2.58                  | -                 | Pd <sup>2+</sup>            | 0.15         | 2.43               |
| 3.64                  | -                 | Pd <sup>2+</sup>            | 0.40         | 3.24               |
| 6.64                  | Pd metal          | Pd metal + Pd <sup>2+</sup> | 1.66         | 4.98               |

For the catalyst with the highest metal content the XPS method and the chemical method gives the same qualitative result. The existence of Pd metal in this polymer is also confirmed by the X-ray diffraction study.

For the other two catalysts the content of Pd metal as determined by the chemical method is indeed very low. Therefore, with the sensitivity that our spectrometer has, only the Pd<sup>2+</sup> part of the total Pd present in the catalysts can be observed with the XPS method. Even for the X-ray diffraction method the content of Pd metal is too low to be detected in all cases but for the catalyst with the highest total palladium content.

The picture derived at by the chemical method also parallels the colour change of the catalysts on activation. The catalyst with the lowest metal content had only a shade of green while the one with highest metal content had changed to grey-green.

From this collected evidence it can rather safely be stated that the chemical method gives an, at least, qualitatively correct, picture i.e. that Pd metal as well as Pd<sup>2+</sup>-phosphine complexes are contained in the resin after activation.

#### B 5. CONCLUDING REMARKS

This study started with the preparation of polymerbound palladium-phosphine coordination catalysts and the testing of them as catalysts for the hydrogenation of soybean oil. In these early investigations marked differences in hydrogenation behaviour was found compared to a similar system with monomeric phosphine ligands. To account for these

anomalies a model of the catalyst was suggested. From a scientific point of view such a model shall, however, not be regarded as true but merely as a guide to new investigations and experiments.

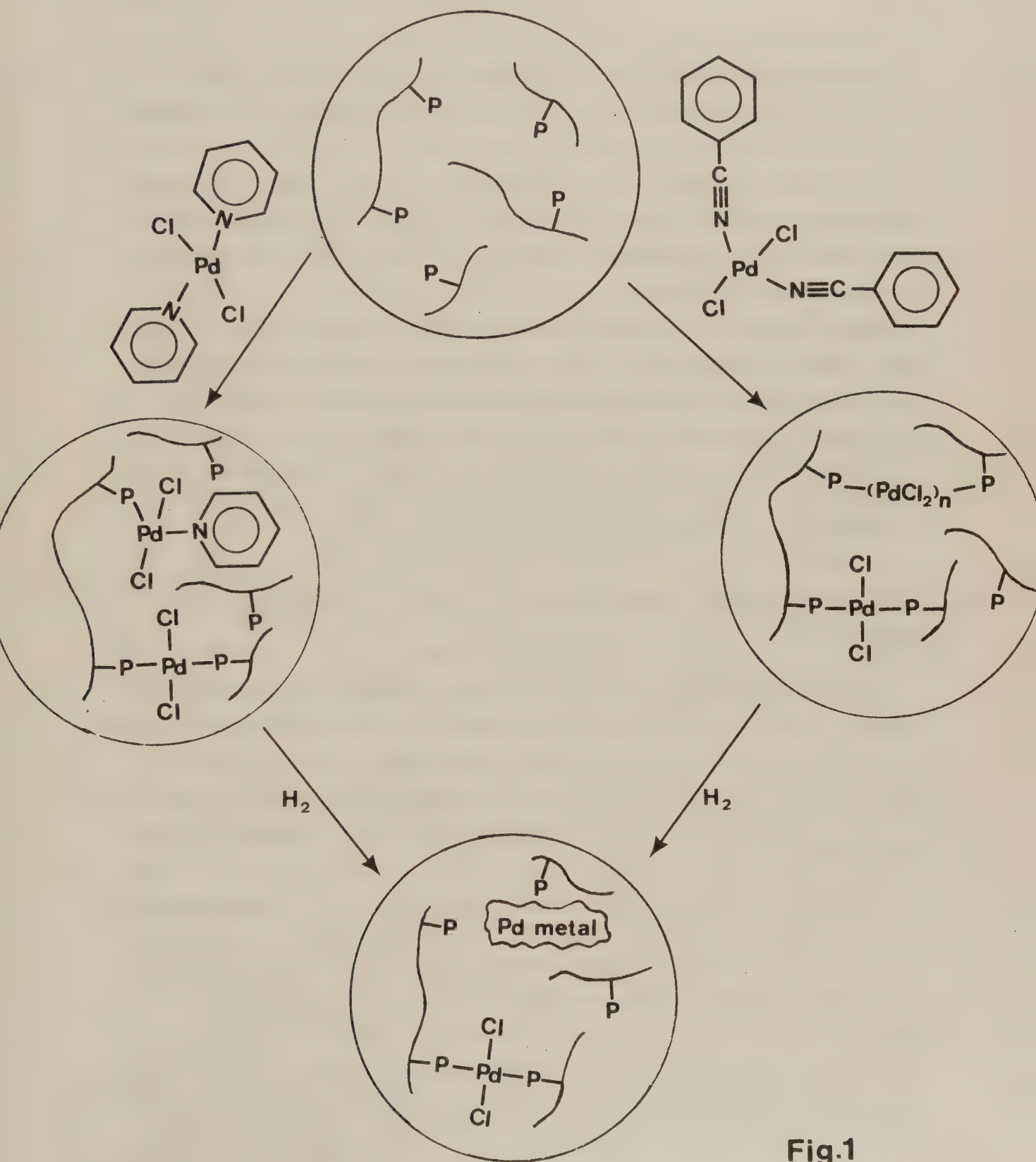


Fig.1



Based on this model several investigations have been performed in the present study. The results of these investigations are that the catalyst system and the reactions it undergoes under reducing condition can be summarized as in fig. 1.

This picture of the catalyst system agrees well with the originally suggested one. No contradicting facts have emerged during this study.

The model has been experimentally confirmed and some complementary details, e.g. the complex  $\text{Cl}_2\text{Pd}(\text{pyridine})(\text{P-PS})$  in the pyridine case and  $\text{PS-P-(PdCl}_2)_n\text{-P-PS}$  in the benzonitrile case, have come forth.

From the point of view of catalysis it is important to have the detailed knowledge of the catalyst system. Only by such knowledge can the catalyst system be changed in a desired direction. Referring to the present system, its catalytic behaviour should most likely be drastically changed if such synthetic procedure were used that prevented the formation of species other than bisphosphine complexes.

#### C. CATALYSTS FOR THE HYDROGENATION TO PRODUCTS WITH LOW TRANS-CONTENT

In the introduction the nutritional demands on the hydrogenation process have been discussed. Such demands are however by no means once and for ever established. On the contrary they change with increased knowledge on how different constituents in the fats are metabolized and incorporated in the human tissue.

During the course of the work reported in the previous part of this study, the discussion (34) on the effect of trans-fatty acids on human health intensified (4). Therefore the search for new catalysts changed to cover also this new aspect.

One type of metal coordination catalyst that previous investigations had shown to give low trans-content in the hydrogenated product was the  $\text{Cr}(\text{CO})$  arene type complexes studied

by Frankel et al. (35, 36, 37). The essential mechanistic feature of this system of homogeneous catalysis can be found in a recent review by Frankel (17). In this connection it may suffice to mention that one intermediate suggested in the mechanism is a bishydride  $H_2Cr(CO)_3$ .

In heterogenous catalysis it has furthermore been found (38) that changes in process variables that increase the surface hydrogen concentration decrease the formation of trans isomers. An increase in hydrogen concentration will presumably lead to a situation  $M - M - M$  or,  $\overset{H}{\underset{|}{M}} - M - M$  where the surface resembles a bishydride metal complex. Based on such observations it was concluded that the search for catalysts with good cis-producing properties should be focused on metal complexes with the ability to form a dihydride complex  $MH_2$ .

Schrock and Osborn have in a number of papers (39, 40, 41) described the catalytic properties of the complex  $NBDRh^+L_2$ , where NBD = norbornadiene and L = phosphine, and established that a dihydride complex  $L_2Rh^+H_2$  is an intermediate in the catalytic cycle. This dihydride complex exists in an equilibrium with a monohydride complex  $L_2Rh^+H_2 \rightleftharpoons H^+ + L_2RhH$  and the equilibrium position can be changed by varying the pH.

This catalyst has therefore been studied for the hydrogenation of soybean oil with the purpose to find out if dihydride complexes are important in the selective hydrogenation of polyunsaturated fats to cis-unsaturated products.

In the present study two different ligands L have been tested i.e. triphenylphosphine and 1,2 bis(diphenylphosphine) ethane (diphos). A marked difference in catalytic activity was noted depending on the phosphine ligand in the complex. The complex with the chelating diphos ligand was found to give a much higher rate of reduction than the complex with the monodentate ligand. In analogy with the findings of Schrock and Osborn (41) the very low rate of reaction with the triphenylphosphine complex was in V supposed to be caused by the formation of nonreactive diolefine complexes,  $L_2Rh^+(diene)_2$ . Chelating ligands like e.g. diphos should according to Schrock and Osborn (41) for steric reasons prevent the forma-

tion of such diolefine complexes. Hence, as also noted in V, a higher rate of reduction should be observed for this ligand.

In an other study (42), published after the present study (V) was submitted for publication, Van der Plank et al. have used similar rhodium complexes with different monodentate ligands, i.e.  $P(C_2H_5)_2C_6H_5$ ,  $P(i-C_4H_9)_3$  and  $P(CH_3)_3$ , as catalysts in the hydrogenation of various fatty acid methyl esters. These authors have found a high catalytic activity for the complexes of the different ligands that they have studied.

That also monodentate ligands can be used to prepare highly active catalysts stands in contrast to the observation and the explanation concerning the triphenylphosphine complex in V. However, it is worth noting that the ligands used in the study of Van der Plank et al. (42) are more basic in nature than triphenylphosphine. In addition to the steric effects, suggested as the cause of the difference between  $P\emptyset_3$  and diphos, also ligand basicity effects might be operating, since the diphos ligand with one alkylgroup is more basic than the triphenyl ligand.

The most interesting part of the results obtained with the cationic rhodium complexes in the present study is the product pattern. With the complex  $NBDRh^+diphos$  the hydrogenation of soybean oil was performed under mild conditions to an iodine value of 80 with not more than  $\sim 10\%$  trans 18:1 in the product. At the same time only very limited amounts of the saturated acid was formed.

When the same catalyst was used with triethylamin added to shift the equilibrium to the monohydride side a totally different product was obtained. In this case high levels of trans acids were formed.

If instead acid was added to the system no change in product pattern was observed compared to that obtained when the catalyst was used without additives.

The mechanistic conclusions drawn from these observations was that two different routes are probably operating.

- 1) The main reaction path includes the coordination of the diene before the thus formed  $L_2Rh^+diene$  complex is



attacked by  $H_2$ . (This route is what is called the C route in the scheme of Schrock and Osborn (41)).

- 2) To account for the effect found on addition of base to the system even the dihydride route, i.e. the addition of  $H_2$  to  $Rh^+L_2$  prior to reaction with the diene, was considered operating to some extent.

It should be mentioned that Halpern in a recent study (43) did not find any evidence for the formation of a dihydride complex  $H_2Rh^+diphos$  in methanol solution. Seemingly this contradicts our interpretation that an addition of base affects the equilibrium  $M^+H_2 \rightleftharpoons MH + H^+$ . However, for getting a conjunction between the A and B reaction routes (41) probably only a small part of the Rh complexes has to be present as dihydride complexes.

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## E. REFERENCES

1. Sabatier, P. and Senderens, J.B., Compt. Rend. 135, (1902) 87.
2. Normann, W., Brit. Pat. 1515 (1903).
3. Lipid Biochemistry, Gurr, M.I. and James, A.T. Chapman and Hall, London, 1971.
4. Symposium on Nutrition Effects of trans fatty acids. Papers presented at the American Oil Chemist's Society Meeting, Chicago, Illinois, USA, September 26-29, 1976, Abstracts 146-150, 159-164, J. Am. Oil Chem. Soc. 53, (1976) 466A-468A.
5. Dutton, H.J. in "Prog. Chem. Fats and Other Lipids" (Holman, R.T. ed.), vol. 9, p. 351, Pergamon, Oxford, 1968.
6. Allen, R.R. and Covey, J.E., Jr., J. Am. Oil Chem. Soc. 47, (1970) 494.
7. Gray, J.I. and Russel, L.F., J. Am. Oil Chem. Soc. 56, (1979) 36.
8. Evans, C.D., Beal, R.E., Mc Connel, D.G., Black, L.T. and Cowan, J.C., J. Am. Oil Chem. Soc. 41, (1964) 260.
9. Unilever, N.V., Dutch Patent Appl. 295, (1963) 863.
10. Koritala, S. and Dutton, H.J., J. Am. Oil Chem. Soc. 43, (1966) 556.
11. Frankel, E.N. and Dutton, H.J., "Topics in Lipid Chemistry", (Gunstone, F.D. ed.), vol. 1, p. 161, Logos Press, London, 1970.
12. Bailar, J.C., Jr. and Itatani, H., J. Am. Oil Chem. Soc. 43, (1966) 377.
13. Bailar, J.C., Jr. and Itatani, H., J. Am. Chem. Soc. 89, (1967) 1592.
14. Itatani, H. and Bailar, J.C., Jr., J. Am. Chem. Soc. 89, (1967) 1600.
15. Itatani, H. and Bailar, J.C., Jr., J. Am. Oil Chem. Soc. 44, (1967) 147.

16. Frankel, E.N., Emken, E.A., Itatani, H. and Bailar, J.C., Jr., J. Org. Chem. 32, (1967) 1447.
17. Frankel, E.N., Rev. Fse. Corps. Gras, 24, (1977) 241.
18. Bailar, J.C., Jr., J. Am. Oil Chem. Soc. 47, (1970) 475.
19. Hartley, F.R. and Vezey, P.N., Adv. Organomet. Chem. 15, (1977) 189.
20. Bruner, H.S., Thesis, University of Illinois, Urbana Illinois, 1971.
21. Bruner, H.S. and Bailar, J.C., Jr., J. Am. Oil Chem. Soc. 49, (1972) 533.
22. Bruner, H.S. and Bailar, J.C., Jr., Inorg. Chem. 12, (1973) 1465.
23. Frankel, E.N. and Little, F.L., J. Am. Oil Chem. Soc. 46, (1969) 256.
24. Awl, R.A., Frankel, E.N., Friedrich, J.P. and Pryde, E.H., J. Am. Oil Chem. Soc. 55, (1978) 577.
25. Collman, J.P., Hegedus, L.S., Cooke, M.P., Norton, J.R., Dolcetti, G. and Marquardt, D.N., J. Am. Chem. Soc. 94, (1972) 1789.
26. Pittman, C.U., Jr., Wu, S.K. and Jacobson, S.E., J. Cat., 44 (1976) 87.
27. Frankel, E.N., Itatani, H. and Bailar, J.C., Jr., J. Am. Oil Chem. Soc. 49, (1972) 132.
28. Michalska, Z.M. and Webster, D.E., Platinum Met. Rev. 18, (1974) 65.
29. Adams, D.M., Goldstein, M. and Mooney, E.F., Trans. Faraday Soc. 59, (1963) 2228.
30. Hartley, F.R., The Chemistry of Platinum and Palladium, Applied Science, London 1973, p. 133.
31. Grubbs, R.H. and Sweet, E.M., Macromolecules, 8, (1975) 241.
32. Grubbs, R.H. and Su, S-C.H., in "Organomet. Polymers" (Carragher, C.E. Jr., Sheats, I.E. and Pittman, C.U. Jr., Eds.) Academic Press, New York, 1978.



33. Terasawa, M., Kaneda, K., Imanaka, T. and Teranishi, S.,  
J. Cat. 51, (1978) 406.
34. Sqoutas, D. and Kummerow, F.A., Am. J. Clin. Nutr. 23,  
(1970) 111.
35. Frankel, E.N. and Little, F.L., J. Am. Oil Chem. Soc. 46,  
(1969) 256.
36. Frankel, E.N. and Butterfield, R.O., J. Org. Chem. 34,  
(1969) 3030.
37. Frankel, E.N., J. Am. Oil Chem. Soc. 47, (1970) 11.
38. Puri, P.S., J. Am. Oil Chem. Soc. 55, (1978) 865.
39. Schrock, R.R. and Osborn, J.A., J. Am. Chem. Soc. 98,  
(1976) 2134.
40. Schrock, R.R. and Osborn, J.A., J. Am. Chem. Soc. 98,  
(1976) 2143.
41. Schrock, R.R. and Osborn, J.A., J. Am. Chem. Soc. 98,  
(1976) 4450.
42. Van der Plank, P., Van der Ent, A., Ondelinden, A.L. and  
Van Oosten H.J., J. Am. Oil Chem. Soc. 57, (1980) 343.
43. Halpern, J., Riley, D.P., Chan, A.S.C. and J.J. Pluth,  
J. Am. Chem. Soc. 99, (1977) 8055.
44. Goggin, P.L. and Mink, J., J.C.S. Dalton Trans. 31, (1974)  
534.

I





# Hydrogenation of Fatty Oils Under Mild Conditions with Palladium-based Coordination Catalyst Anchored to Organic Polymer Matrices

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## Abstract

*Hydrogenation of fatty oils under mild conditions with palladium-based coordination catalyst anchored to organic polymer matrices.* Andersson, C.; Larsson, R. (Division of Inorganic Chemistry I, Chemical Center, University of Lund, P.O. Box 740, S-220 07 Lund, Sweden.)

A polymer anchored coordination catalyst has been synthesised by reacting  $\text{Cl}_2\text{Pd}(\text{NC}_6\text{H}_5)_2$  with phosphinated polystyrene. This catalyst has been used for the hydrogenation of soybean oil under mild conditions (1 atm.  $\text{H}_2$  pressure and temperatures in the range 80–140°C). The catalyst was found to be effective and selective for the hydrogenation of the polyene fraction of the oil even in absence of solvent. A temperature dependent induction period for the catalytic reaction, that is connected with a colour change of the catalyst was found. The activation of the catalyst is discussed in terms of reduction of  $\text{Pd}^{2+}$ . A model with two different active sites is proposed.

## Introduction

Insoluble polymer supports have in recent years been widely used to immobilise transition metal complexes normally used as homogeneous catalysts. For reviews see Ref. [1, 2, 3, 4]. The main purpose of research in this field is to find ways to combine the advantages of homogeneous catalysis, such as high activity and selectivity, and heterogeneous catalysis, ease of catalyst separation and reuse of catalyst.

The  $\text{ML}_2\text{X}_2$  type complexes, where M is Pt, Pd or Ni and L is a phosphine ligand, are some of the most thoroughly investigated catalysts for homogeneous hydrogenation of polyunsaturated fats.

Bruner and Bailar [5, 6] have shown the possibility of fixing these catalysts on porous polymer support through phosphine links. They studied these anchored complexes as catalysts for the hydrogenation of fatty acid methyl esters in solution. Their results on the Pt system are in accord with previous results [7]. For the Pd system however they found that in addition to high selectivity for polyene compounds, the fixed catalyst shows higher activity under much milder conditions than its homogeneous analog.

These results on the Pd-system have prompted us to investigate the Pd-system under more industrial-like conditions i.e. hydrogenations of refined soybean oil without solvent. This simplifies the operations as solvent separation will not be necessary.

## Experimental

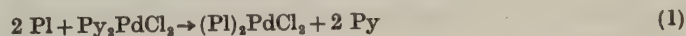
**Materials:** Analytical grade chemicals and solvents were used throughout this work without further purification. Refined bleached soybean oil was a gift from AB Karlshamns Oljefabriker.

Chloromethylated polystyrene with 2 % crosslinking and a chlorine content of 4–5 % was purchased from Merck (Merri-field Harz, art 805064).

$\text{Cl}_2\text{Pd}(\text{pyridine})_2$  was prepared by standard procedure i.e. treating a water solution of  $\text{PdCl}_2$  with pyridine and recrystallizing the product from  $\text{CH}_2\text{Cl}_2$ /light petroleum mixture.

**Catalyst preparation:** The chloromethylated polystyrene was reacted with a solution of  $\text{LiPPh}_2$ , generated from Li metal and triphenylphosphine, in dry THF [8].

This phosphinated polymer further referred to as PI has a phosphorus content of 1.1 mmol/g polymer based on difference in chlorine content before and after  $\text{PPh}_2^-$  treatment. Ligand exchange according to eq. (1).



was employed to prepare polymer bound palladium.

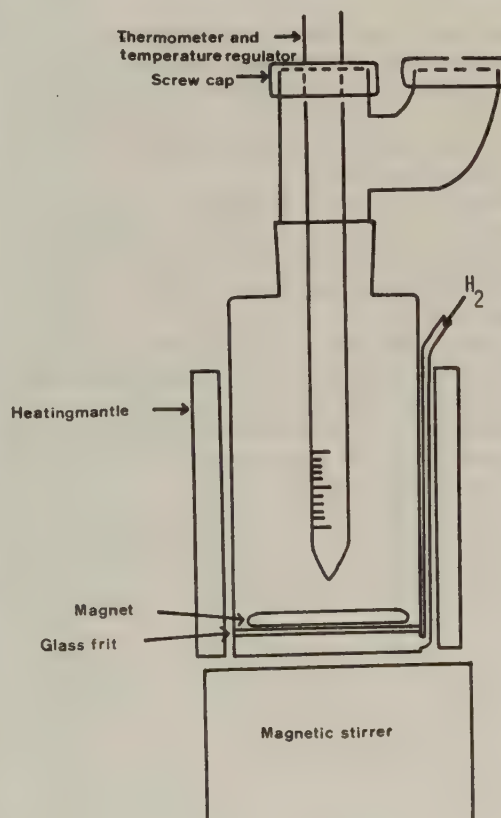


Fig. 1. A schematic drawing of the catalytic hydrogenation apparatus.

This ligand exchange reaction was performed at room temperature by shaking a solution of  $\text{Cl}_2\text{PdPy}_2$  in  $\text{CH}_2\text{Cl}_2$  with stoichiometric amount of PI.

By using  $\text{CH}_2\text{Cl}_2$ , a solvent where the polymer swells well and so makes all the phosphorus inside the polymer easily accessible, the ligand exchange was completed within a few hours, as could be seen by the decolouration of the yellow methylchloride solution.

The resulting light yellow polymer was washed with acetone and then extracted with  $\text{CH}_2\text{Cl}_2$  in a soxhlet apparatus to remove traces of unreacted material.

#### Hydrogenations

The hydrogenation experiments were performed on bleached refined soybean oil in an apparatus as depicted in Fig. 1. The reactor was loaded with catalyst and oil while a slow stream of nitrogen was maintained. When the desired temperature was reached the first sample was withdrawn (this defines  $t = 0$ ) and the nitrogen gas was changed for hydrogen. The hydrogen flow was set to a specified value. At regular time intervals samples were withdrawn with a syringe.

The catalyst was separated from the liquid oil by centrifugating the samples and the oil was analyzed.

#### Analysis

After methylation of the oil samples they were glc analyzed on a 6 feet SS SP-216-PS column using a PE F17 gas chromatograph equipped with flame ionisation detection. The iodine numbers were calculated from the composition of the samples as determined by glc.

The palladium content was analyzed as follows: Palladium containing polymers were oxidized to complete destruction by a mixture of sulfuric acid and hydrogen peroxide. The resulting solutions were analyzed for Pd by atomic absorption spectrometry.

#### Results and discussion

Homogeneous catalysis — as the name indicates — is performed with substrate and catalyst dissolved in a suitable solvent to achieve a homogeneous mixture. Up to now fat hydrogenation on industrial scale is a heterogeneous process, which is run batchwise with the catalyst suspended in the substrate (the oil) as small particles.

With immobilised homogeneous catalyst the problem of catalyst separation and recovery can be solved in the same manner as for traditional heterogeneous catalysts. Another consequence of the immobilisation is that there is no need of a solvent to dissolve the catalyst.

Sometimes the role of the solvent in homogeneous catalysis is not only to dissolve the catalyst and the substrate but also to function in various other ways.

In some homogeneous systems the solvent plays the role of a ligand which takes part in the catalytic cycle by alternating coordination and noncoordination [9].

It has been shown [6] by deuterium labelling studies that the alcoholic proton in methanol used as solvent for experiments with polymer anchored Pd-complexes can function as a source for hydride ions and thereby influencing the hydrogenation mechanism.

The swelling capacity of the polymer and accordingly the accessibility of the catalytic centers inside the polymer depends on the properties of the solution in which the catalyst is suspended. This is another possible way in which the solvent can influence the function of polymer anchored complexes.

With these possible ways of solvent influence in mind the results shown in Fig. 2 are interesting. These were obtained with 0.5 gram  $\text{PdCl}_2(\text{PI})_2$  suspended in 100 ml soybean oil at  $120^\circ\text{C}$ , with a hydrogen flow of 250 ml/min at atmospheric

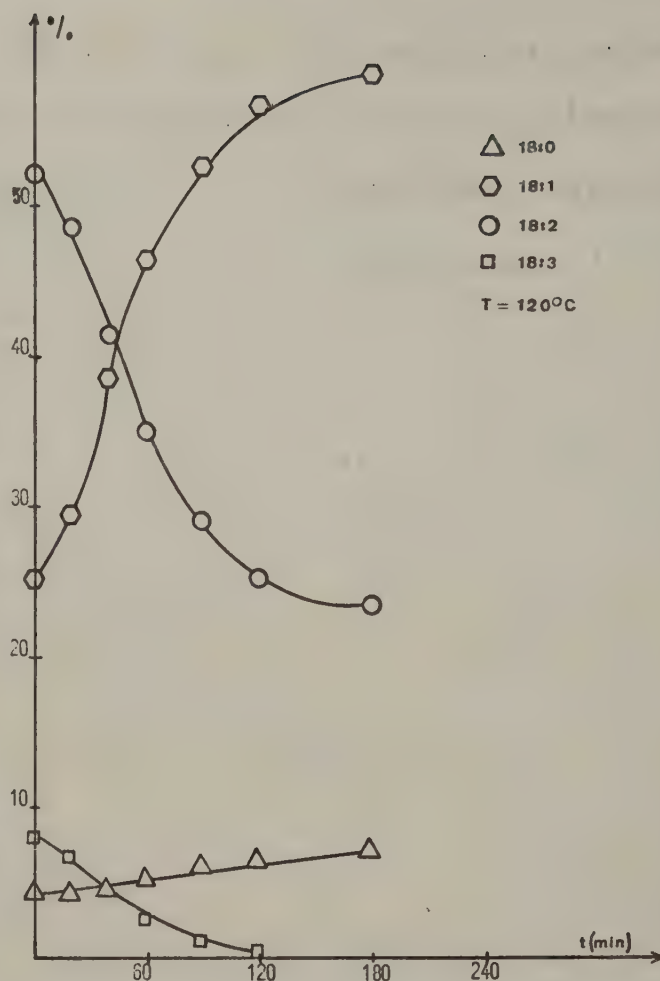


Fig. 2. Rate of hydrogenation of soybean oil catalyzed by the polymer anchored palladium — phosphine catalyst in absence of solvent at 1 atm  $\text{H}_2$  pressure and  $120^\circ\text{C}$ .

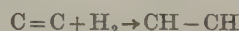
pressure. As can be seen, the solvent is not necessary for the catalyst to show high activity and high selectivity for polyene. The reduction of the triene and diene fractions is fast (complete reduction of 18:3 within 120 min), while the increase in saturated acid is small.

The technique of immobilising homogeneous catalysts on a support, can thus make it possible to use transition metal complexes as catalysts in much the same way as heterogeneous catalysts are used today.

The need for higher hydrogen pressure (550 psi,  $70^\circ\text{C}$ ), when working without alcoholic solvents [6], has been compensated for by a somewhat higher reaction temperature (1 atm,  $120^\circ\text{C}$ ).

#### Catalyst activation

In Fig. 3 the iodine number versus time is plotted for a series of experiments conducted at different temperatures with the polymer bound catalyst. The change in iodine number with time gives little information of the selectivity. It is merely a measure of the ability of the catalyst to catalyse the reaction



At low temperature ( $80^\circ$ ) the catalytic activity as depicted in Fig. 3 is nearly zero at the beginning (120 min) and then a slow reaction starts. A similar but shorter induction period is noticeable at  $100^\circ\text{C}$ .

This induction period for the catalytic reaction is directly connected with a colour change of the catalyst, from light yellow to grey-green (also noted earlier [6, 10]).



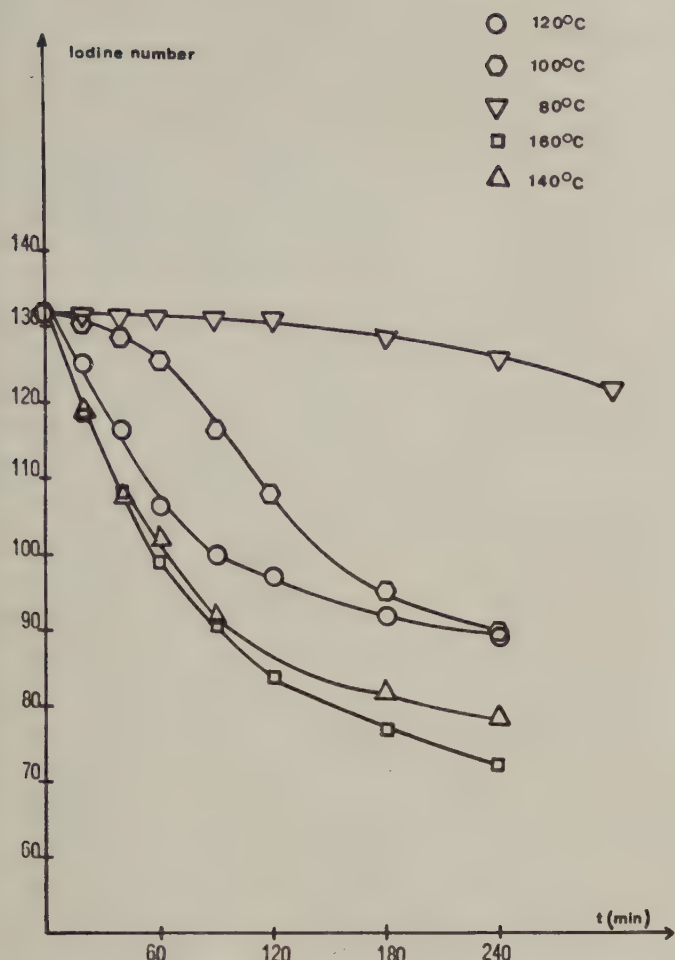
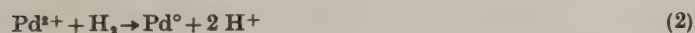


Fig. 3. The catalytic activity and the activation of the catalyst at different temperatures.

At 120°C or at higher temperature the colour change takes place at once and the catalytic reaction starts from  $t=0$ . This is a direct evidence for some kind of change within the polymer-bound phosphine-palladium complex, under these conditions (temp,  $H_2$ ) whereby species of low catalytic activity are converted to such ones of higher catalytic activity.

The simplest way to explain the changes leading to the green, high-active catalyst is to assume a reduction of  $Pd^{2+}$  to Pd metal as shown in eq. (2).



This is a normal way of producing a supported metallic Pd catalyst. The situation within the phosphine containing polystyren support is, however, different in one respect. The  $Pd^{2+}$  in this case is not adsorbed on the support, but covalently bound through phosphine links to the support. These covalently bound phosphine ligands are known to be able to stabilize the metal in low oxidation states through  $\pi$ -back donation. The phosphine ligands "prevent" the reduction of palladium to the metallic state.

The possibility of reduction to the metallic state was ruled out by Brunner and Bailar through a  $Pd^{2+}$  removal operation test [6]. Treatment of the used, green polymer with  $CN^-$  should remove all  $Pd^{2+}$  present leaving only Pd metal if any on the polymer. By doing so they caused their polymer to change to the white colour of the free ligand PI. This  $CN^-$  treated polymer was found to be inactive as catalyst. We have similarly treated our green, used polymer with  $CN^-$  with the same result.

We have found that if the polymer catalyst is treated with hydrazine in ethanol the colour changes as when the catalyst is used for hydrogenation. Bearing in mind that hydrazine is a reducing agent this effect supports an explanation that

the colour change is caused by some kind of reduction. This reduction does not have to be a reduction from  $Pd^{2+}$  to Pd metal however. Hydrazine reduction is often used to synthesize hydrido complexes and zerovalent palladium phosphine complexes.

In order to compare the hydrogenation characteristics of  $Cl_2Pd(PI)_2$ , hydrazine treated  $Cl_2Pd(PI)_2$  and commercial Pd on carbon catalyst (10 % Pd) the three catalysts have been used under identical conditions (140°C, 250 ml  $H_2$ /min) with the same metal to oil ratio. The results are shown in Fig. 4. With Pd on carbon catalyst the reaction course is different from that of polymer bound palladium phosphine complexes. While the Pd on carbon catalyst shows the same rate of reaction down to a IN of 30, the reaction rate for both the polymerbound catalysts decreases when an iodine value in the region of 100 is reached. This decrease in reaction rate can be explained by catalyst selectivity: The rate of reduction of monoene is slower than that of polyene.

Hence the Pd on carbon catalyst does not show the selectivity shown by the polymer bound palladium catalyst, when used under the same conditions.

The difference in polyene selectivity between hydrazine treated  $Cl_2Pd(PI)_2$  and in situ reduced  $Cl_2Pd(PI)_2$  on one hand and Pd on carbon catalyst on the other can be explained in terms of different active sites. Another possible explanation is the difference in support.

Pd on carbon has Pd metal as the active species. The nature of the catalytic active species on the polystyrene bound catalyst is difficult to determine. One type of species that seems possible

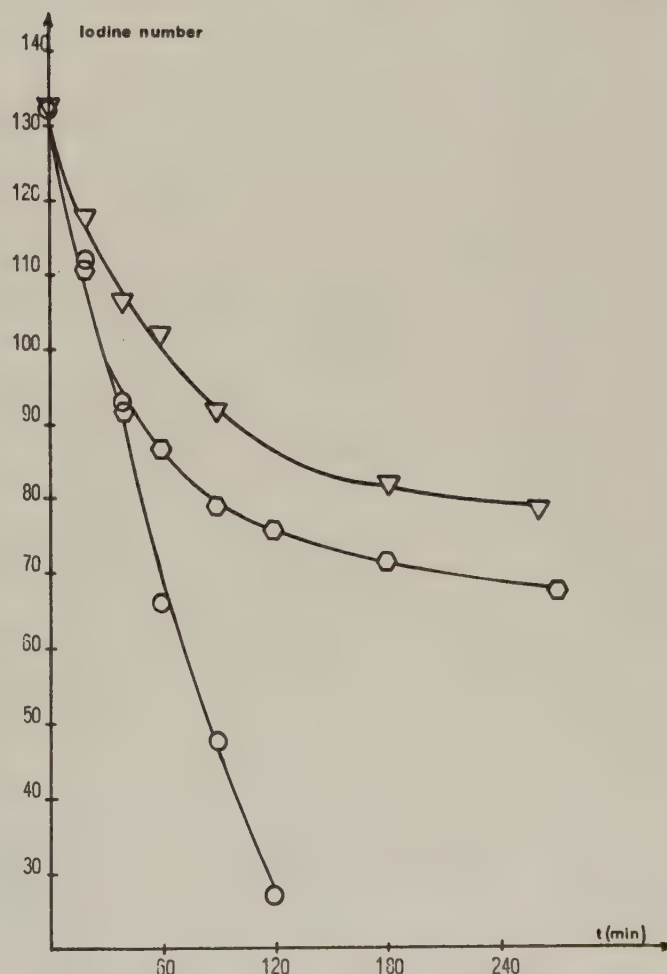


Fig. 4. A comparison of the catalytic activity under identical conditions (1 atm  $H_2$ , 140°C) between  $\nabla$   $Cl_2Pd(PI)_2$ ,  $\circ$   $Cl_2Pd(PI)_2$  treated with hydrazine and  $\bigcirc$  Pd on carbon.



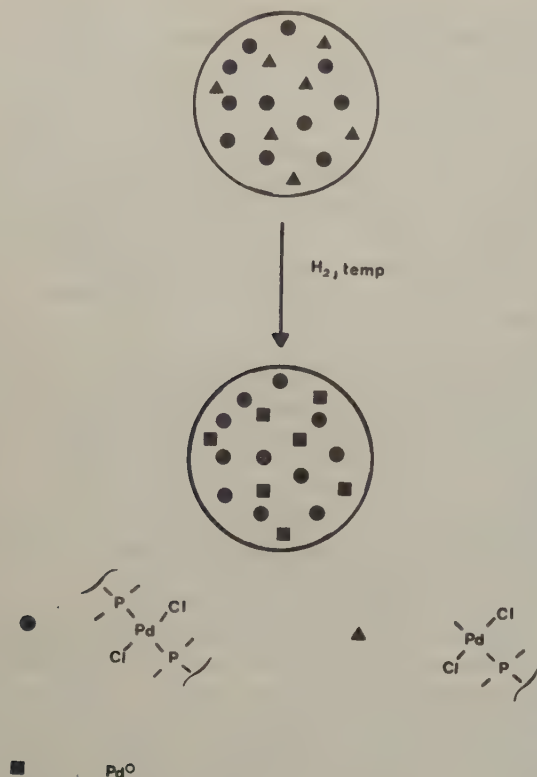


Fig. 5. Proposed model for the polymer anchored catalyst with two different sites and activation under reaction conditions.

is some kind of low valent Pd–P cluster, formed under the reducing conditions.

Another, perhaps more attractive model for the catalytic active centers in the polystyrene catalyst that takes into account both the results from the  $\text{CN}^-$  treatment and the reducing conditions that causes the colour change, is the following.

Due to local deficit of phosphine within the polymer some  $\text{Pd}^{2+}$  atoms are not coordinated to two phosphine ligands but are coordinated in some other way.

These  $\text{Pd}^{2+}$  atoms that do not carry two phosphine ligands are susceptible to reduction and the result under reducing conditions is a catalyst with a structure as shown in Fig. 5.

Such a catalyst with both metallic Pd and phosphine bound  $\text{Pd}^{2+}$  complex has in fact two active centers that can function in different ways.

The metallic Pd helps in activating  $\text{H}_2$ . This explains the difference in reaction conditions necessary for polymer-bound  $(\text{Pl})_2\text{PdCl}_2$  catalyst (atm pressure) on one hand and  $(\text{PR}_3)_2\text{PdCl}_2$  on the other.

On the  $(\text{Pl})_2\text{PdCl}_2$  sites the olefin is activated and the hydrogenation completed. This explains the hydrogenation behaviour i.e. the polyene selectivity, as distinguished from Pd on carbon catalyst.

If this two-center catalyst is treated with  $\text{CN}^-$  all the  $\text{Pd}^{2+}$  is removed and the Pd metal still remaining is not capable of catalysing the hydrogenation.

Attachment of homogeneous catalyst to polymer phosphine ligands can bring about the following desirable effects: 1) ease of catalyst separation, 2) non-requirement of solvents, 3) re-use of catalyst. A negative effect that follows from the heterogenization is the difficulty to study and determine the actual catalytic active species.

In the case of the polymer bound Pd catalyst used in this study we feel that further studies, are necessary to reveal the true nature of the system.

## Acknowledgements

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## References

1. Michalska, Z. M. and Webster, D. E., *Platinum Met. Rev.* 1974, 18, 65.
2. Bailar, J. C., *Cat. Rev. Sci. Eng.* 1974, 10, 17.
3. Cernia, E. M. and Graziani, M., *J. Appl. Polym. Sci.* 1974, 18, 2725.
4. James, B. R., *Homogeneous Hydrogenation*, Wiley, New York, 1976.
5. Bruner, H. S. and Bailar, J. C. Jr., *J. Am. Oil Chem. Soc.* 1972, 49, 533.
6. Bruner, H. S. and Bailar, J. C. Jr., *Inorg. Chem.* 1973, 12, 1465.
7. Bailar, J. C., Jr., *J. Am. Oil Chem. Soc.*, 1970, 47, 475.
8. Kosolapoff, G. M. and Maier, L., *Organic Phosphorus Compounds*, Vol. 1, Wiley, New York, 1972.
9. Coates, G. E., Green, M. L. H., Powell, P. and Wade, K. *Principles of organomet. chem.*, Methuen and Co LTD, London 1971, page 237.
10. Bruner, H. S., Thesis University of Illinois, Urbana, Illinois.

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II





Investigations on the conditions for hydrogenation of fatty  
oils with polymer anchored Pd-phosphine complexes

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Running title: Hydrogenation of fatty oils with Pd-phosphine  
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investigations on the conditions for hydrogenation of  
fatty oils with polymer anchored Pd-phosphine complexes

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ABSTRACT

Palladium chloride has been anchored to phosphinated cross-linked polystyrene by substitution of the pyridine ligand in  $\text{Cl}_2\text{Pd}(\text{NC}_5\text{H}_5)_2$  with the polymeric phosphine. By analytical and infrared studies of the prepared catalyst it has been shown that the main species formed in the matrix is the half-substituted complex  $\text{Cl}_2\text{Pd}(\text{NC}_5\text{H}_5)\text{P-PS}$  (P-PS = polymeric benzyldiphenyl(phosphine)). This polymer bound palladium complex has been tested together with two other preparations, both of which are bisphosphine complexes, as catalyst for hydrogenation of soybean oil. The result from this test shows that the presence of the mixed phosphine-pyridine complex is necessary for catalytic activity under ambient conditions. The monoene fraction of the oil is hydrogenated very slowly, but the polyene fraction is reduced quickly. Relatively large amounts of trans-isomers are however formed on the reaction. It has been noted that the activation of the catalyst is coupled to a release of pyridine from the catalyst. It is proposed that after the release of pyridine further reactions take place inside the polymer which cause the catalyst to be active under mild conditions.

## INTRODUCTION

Since the pioneering work by Haag and Whitehurst (1), much research has been carried out on the attachment of homogeneous transition metal catalysts to insoluble supports. A number of recent reviews covering this topic have also been published (2, 3, 4, 5). The main reason for heterogenizing a homogeneous transition metal catalyst lies in its easier handling, i.e. its removal, recovery and recycling.

For the homogeneous hydrogenation of unsaturated fatty acids three types of complexes have been more thoroughly investigated (6). Bailar and coworkers (7, 8, 9, 10) have studied the  $X_2ML_2$ -type complexes ( $M = Ni, Pd, \text{ or } Pt$  and  $L$  is a phosphine ligand.) These complexes, proved to be very selective for polyene hydrogenation. Frankel has studied iron carbonyl complexes (11, 12, 13, 14) and  $Cr(CO)_3$  arene complexes (15, 16, 17, 18, 19) as catalysts. The Cr complexes have been shown to give very low trans-content in the hydrogenated product.

The polyene selectivity of all these complexes and low concentration of trans-products found for the Cr-complexes are essential features of these catalysts that could conveniently be used to make products of specific quality. In spite of this none of these complexes have gained industrial application, mainly because of the great separation problem. However, by using polymer anchored complexes as catalysts one should be able to overcome the problem of separation and thereby take advantage of the high polyene selectivity and low trans-formation, where such is found.



Pittman (20) has shown the possibility to immobilize carbonyl complexes through CO-phosphine exchange. In this way it should be possible to anchor  $\text{Fe}(\text{CO})_5$ . Pittman (21a) has also synthesized polymer bound  $\text{Cr}(\text{CO})_3$ -arene complexes but did not use them for fatty acid hydrogenation purposes. Ayl et al. (21b) have synthesized similar polymer-bound  $\text{Cr}(\text{CO})_3$ -arene complexes and used these as catalysts in the hydrogenation of soybean oil and esters. Bailar and Bruner (22, 23) have synthesized  $\text{PdCl}_2$  and  $\text{PtCl}_2$  bound to polymeric phosphine ligands and used these as catalysts for the hydrogenation of soybean oil methyl esters. We (24) have extended their work on  $\text{PdCl}_2$  and found it to be a good catalyst for soybean oil hydrogenation. The polymer bound  $\text{PtCl}_2$  catalyst used by Bailar and Bruner (22, 23) was found to give essentially the same hydrogenation behavior as the nonsupported catalyst. For the Pd-system, however, the situation is different (22, 24). Marked differences between homogeneous and polymer bound Pd-phosphine complexes are found. The essential features of these are summarized in table 1.

Differences between homogeneous and polymer catalysts in activity and selectivity have sometimes been noted (25, 26). For the so called Wilkinson catalyst  $\text{ClRh}(\text{P}\phi_3)_3$  these differences are often explained in terms of the position of the phosphine dissociation equilibrium



For other systems (27) the polymer ligand has prevented an unfavorable aggregation of catalytic species and so increased the catalytic activity of the anchored complex, compared to the homogeneous complex.

The reason for increased catalyst activity when  $\text{PdCl}_2$  is anchored to a polymeric phosphine ligand is presumably not possible to find in terms of the above mentioned phosphine dissociation equilibrium or a hindered aggregation. Pittman (28) has used polymer-bound palladium phosphine complexes to oligomerize 1,3-butadiene, and noted the same color change as we do (see table 1). These authors ascribe this color change to the deposition of metallic Pd. However, the reduction to Pd metal was ruled out by Bruner and Bailar (23).

Under the reaction conditions we have used, monomeric  $\text{Cl}_2 \text{ Pd} (\text{P}\phi_3)_2$  has been found to be stable to reduction. If the change of the catalytic activity depends on the formation of metallic Pd in the matrix, this must derive its origin from species other than  $\text{Cl}_2 \text{ Pd}(\text{P-PS})_2$ , (P-PS = polymeric benzyl-diphenyl phosphine) within the matrix.

The aim of the present work has been to investigate the

species formed, when  $\text{PdCl}_2$  is anchored to phosphinated polystyrene - divinyl benzene polymers. By doing this we hoped to be able to throw some light on the question of the possible formation of metallic Pd.

## EXPERIMENTAL

Materials: Analytical grade chemicals and solvents were used throughout this work without further purifications. Refined bleached soybean oil was a gift from AB Karlshamns Oljefabriker. Chloromethylated polystyrene with 2% crosslinking and a chlorine content of 4-5% was purchased from Merck (Merrifield Harz, art.nr 805064).

$\text{Cl}_2\text{Pd}(\text{NC}_5\text{H}_5)_2$  was prepared by standard procedure i.e. treating a water solution of  $\text{PdCl}_2$  with pyridine and recrystallizing the product from  $\text{CH}_2\text{Cl}_2$ /light petroleum mixture.

$\text{Cl}_2\text{Pd}(\text{NC}_5\text{H}_5)\text{P}\phi_3$  was prepared by reacting  $\text{Cl}_4\text{Pd}_2(\text{P}\phi_3)_2$  with pyridine according to the procedure of Chatt (29).

## Phosphination

The chloromethylated polymer was treated first with 1N HCl, then with 1N NaOH and thereafter washed successively with water, methanol, 1:1 methanol:  $\text{CH}_2\text{Cl}_2$ , and finally with pure  $\text{CH}_2\text{Cl}_2$  and dried at  $80^\circ\text{C}$  and 2 Torr for 24 hours. This dried polymer was then, made to react with a slight excess of  $\text{Li P}\phi_2$  generated



from Li metal and  $P\phi_3$  (30) in THF, (tetrahydrofuran), under  $N_2$ . After at least 24 hours, unreacted  $LiP\phi_2$  was hydrolyzed by the addition of ethanol. The polymer was recovered by filtration. It was then washed with water, ethanol, THF and finally extracted in a Soxhlet apparatus with acetone for 6 hours and with  $CH_2Cl_2$  for 18 hours before drying. Analysis of this polymer gave 1.8% P corresponding to 0.58 mmol P/g.

### Catalysts preparations:

#### Catalyst 1

This was prepared by the procedure of Bruner and Bailar (22,23) i.e. exchanging an N-donor ligand with the polymeric phosphine ligand. As N-donor ligand we have chosen pyridine instead of benzonitrile. The procedure was as follows:

$Cl_2Pd(NC_5H_5)_2$  (2.1 g, 6.2 mmol) dissolved in  $CH_2Cl_2$  was reacted under nitrogen with the phosphinated polystyrene (20 g, 11.6 mmol) for 24 hours at room temperature. The resulting yellow polymer was then collected by filtration and finally extracted with  $CH_2Cl_2$  for 24 hours in a Soxhlet apparatus. Analysis gave 3.10% Pd and 0.33% N corresponding to 0.29 mmole Pd/g and 0.24 mmole N/g. The filtrate from the reaction was analyzed for released pyridine.

Calculated (for a release of 2 mole of pyridine per mole of Pd incorporated in the polymer):

12.4 mmol

Found:

7.8 mmol

Difference:

4.6 mmol

This difference corresponds to 0.23 mmole pyridine still remaining on each gram of the prepared catalyst.

### Catalyst 2

A solution of  $\text{Cl}_2\text{Pd}(\text{P}\phi_3)_2$  (0.70 gram, 1 mmol) in  $\text{CH}_2\text{Cl}_2$  (200 ml) was stirred at reflux under  $\text{N}_2$  atmosphere with the phosphinated polymer (2 g, 1.2 mmol P) for 48 hours. This was then filtered and extracted as catalyst 1.

Analysis of this preparation gave 1.36% Pd corresponding to 0.13 mmole Pd/g.

### Catalyst 3

This catalyst was prepared by reacting catalyst 1 (2.0 g, 0.58 mmol Pd) with a solution of  $\text{P}\phi_3$  (0.16 g, 0.6 mmol) in  $\text{CH}_2\text{Cl}_2$  (25 ml). After 12 hours treatment the polymer was separated and extracted in the same way as catalyst 1.

Analysis of this catalyst gave 1.20% Pd (0.11 mmol/g) and no measurable content of N.

Analysis of the filtrate for released pyridine gave 0.48 mmol of pyridine. This value corresponds to 0.24 mmol pyridine per gram of the catalyst 1.

### Analytical procedures:

To analyze the amount of phosphorous and palladium in the polymer catalysts, the organic polymer had to be completely oxidized. This was done with  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$  according to the following procedure:

To 50 mg of finely ground polymer a few drops of concentrated sulphuric acid was added. After allowing the polymer to be thoroughly wetted by the acid, the sample was heated gently on an open flame until the polymer no longer was floating. When the mixture was cold a few drops of hydrogen

peroxide (30 %) was added and the mixture heated on an oil bath at 80°C. The addition of hydrogen peroxide was continued until complete dissolution and discoloration of the solution occurred. The mixture was heated at 150°C overnight to remove traces of unreacted hydrogen peroxide.

Phosphorous was determined as phosphate. This was done spectrophotometrically by a molybdenum blue method, using ammonium molybdate and amidol as reagents (31). Analysis of phosphorous was done on phosphinated polymers before metal fixations. Palladium was determined by atomic absorption spectrometry.

GLC-analysis of released pyridine in the filtrates from the catalyst preparations was done on a BDS column with octanol as internal standard.

Coordinated pyridine was analyzed as elementary nitrogen (Microanalytical Laboratory, University of Lund).

#### Hydrogenations:

All hydrogenations were performed on bleached refined soybean oil at atmospheric pressure in an apparatus as depicted in fig. 2. The reactor was loaded with soybean oil and catalyst while a slow stream of nitrogen was maintained. The reaction vessel was heated and when the desired temperature was reached the first sample was withdrawn ( $t=0$ ) and the nitrogen gas was changed for hydrogen. The hydrogen flow was kept at a fixed value. At regular time intervals samples were withdrawn with a syringe.

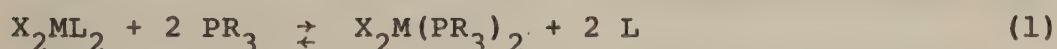


The catalyst was separated from the oil by centrifugating the samples. After converting the oil samples to methyl esters, these were analyzed on a 6 feet SS SP-216 PS column using a PE Fl7 gas chromatograph equipped with flame ionization detection. Trans content was determined by IR spectroscopy (32).

## RESULTS AND DISCUSSION

### The catalysts

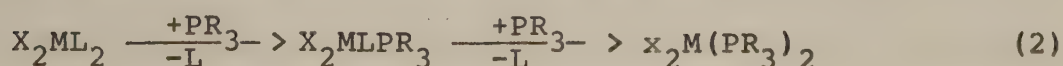
Ligand substitution according to the equation



(where L represents an N-donor ligand) is a convenient way to prepare palladium phosphine complexes. When monomeric phosphine ligands such as triphenylphosphine are used the equilibrium lies far to the right and substitution is quantitative.

This facile substitution reaction has also been applied to phosphinated styrene divinylbenzene polymers as ligands (23, 24). Even in this case the substitution seems to proceed according to eq 1 as judged by the complete discoloration of the yellow solution, when a stoichiometric ratio of Pd:P is used.

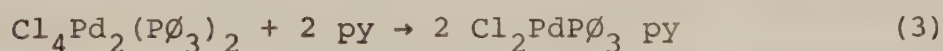
Substitution according to equation 1 must be assumed to proceed as a two-step process with successive substitution of the N-donor.



In an effort to explain the differences in catalytic behavior (table 1) between the homogeneous catalyst  $\text{Cl}_2\text{Pd}(\text{P}\emptyset_3)_2$  and the polymer anchored complex  $\text{Cl}_2\text{Pd}(\text{P-PS})_2$ , we have investigated the substitution reaction in greater detail.

### Catalyst 1

Analyses of the filtrate for displaced pyridine and total nitrogen clearly indicate that with this polymer phosphine ligand the substitution is not complete. The reaction does not proceed much further than corresponding to the first step in eq. 2. The main species formed would thus have structure II proposed in figure 1. The reason for formation of the half-substituted species II in fig 1 is probably best explained in terms of the stability of species II and the separation and mobility of the phosphine groups in the matrix. An analog to the half-substituted species can be prepared and isolated by reacting a dimeric chlorine bridged phosphine complex with pyridine (see Experimental).



This mixed pyridine-phosphine complex is stable and does not disproportionate to bisamine and bisphosphine complexes as does similar complexes with sulphur, selenium or tellurium.

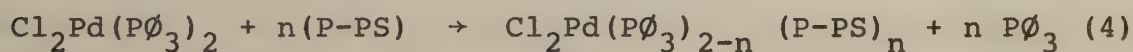
In the styrene-divinyl benzene matrix, only about 10% of the benzene rings are substituted with phosphine groups. This means that the styrene chains has to bend to bring the phosphine groups closer together. If the repulsive energy that develops for steric reasons when the styrene chains bend, is greater than the energy gained by substitution of the second

pyridine ligand, the substitution is stopped after the first step in equation (2). Some of the phosphine groups are, however, located so that reaction according to equation 1 also will occur. This can be seen by the ratio  $\text{Pd/N} = 1.21 > 1$ .

The analysis of catalyst 1 indicates thus, that the species 1 expected from eq. 1 is only formed to a minor extent. Instead species II will be the major product in the matrix.

### Catalyst 2

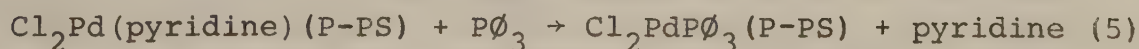
Catalyst 2 was prepared by reacting  $\text{Cl}_2\text{Pd}(\text{P}\phi_3)_2$  with the polymeric phosphine ligand in  $\text{CH}_2\text{Cl}_2$



Although an excess of  $\text{Cl}_2\text{Pd}(\text{P}\phi_3)_2$  was used the equilibrium position for this reaction is such that only a small quantity of palladium was incorporated in the polymer. The palladium in this catalyst is however coordinated to two phosphines. From a comparison between catalyst 1 and 2 it should be possible to obtain some information as to whether or not species II formed in catalyst 1 is responsible for the changed catalytic behavior.

### Catalyst 3

This catalyst was prepared by treating catalyst 1 with  $\text{P}\phi_3$ , hoping for the reaction (5) to proceed.





This pyridine - triphenylphosphine exchange was, however also followed by some Pd leaching from the polymer, probably due to the formation of  $\text{Cl}_2\text{Pd}(\text{P}\emptyset_3)_2$ . Therefore the amount of palladium in this catalyst is lower than in catalyst 1. This Pd leaching is probably caused by a greater tendency of Pd to coordinate to  $\text{P}\emptyset_3$  compared to P-PS. The basis for this suggestion is the result obtained on synthesis of catalyst 2. The equilibrium position in the preparation of catalyst 2 (eq. 4) is such that the left side is favored and a nearly equal amount of Pd is coordinated in catalyst 2 and 3.

In spite of these complications the treatment of catalyst 1 with  $\text{P}\emptyset_3$  results in a catalyst containing only bisphosphine complexes. (The amount of pyridine released on  $\text{P}\emptyset_3$  treatment 0.24 mmole/g equals to the amount of pyridine calculated from N-elementary analysis of catalyst 1). This  $\text{P}\emptyset_3$  treatment gives thus yet another possibility to study the catalytic effect of the phosphine-pyridine complex  $\text{Cl}_2\text{Pd}$  pyridine (P-PS) compared to the bis-phosphine complex.

### IR-spectra

To get further evidence for the formation of species II in the preparation of catalyst 1 IR spectra were recorded for all the prepared catalysts. The spectra of catalyst 2 and 3 show no peaks that can not be identified in the spectra of either the matrix or  $\text{Cl}_2\text{Pd}(\text{P}\emptyset_3)_2$  in the region  $4000 - 400 \text{ cm}^{-1}$ .

In the spectra of catalyst 1 a weak shoulder at  $1220 \text{ cm}^{-1}$  is present (see fig 3). This signal corresponds to a very sharp

peak at the same wavelength in the spectra of  $\text{Cl}_2\text{Pd py}(\text{P}\emptyset_3)$ , that is not present in either the matrix or  $\text{Cl}_2\text{Pd}(\text{P}\emptyset_3)$  spectra. Also in other regions of the spectra significant similarities to the spectrum of  $\text{Cl}_2\text{Pd py}(\text{P}\emptyset_3)$  can be found. Therefore this spectrum of catalyst 1 strengthens the evidence for formation of species II.

## HYDROGENATIONS

The three different preparations were tested as catalyst for the hydrogenation of soybean oil. The same mild reaction conditions were used for these tests as previously used with polymer-bound  $\text{PdCl}_2$  (24) i.e. atmospheric pressure and temperatures in the range 80-140°C. In figure 4 the product composition as a function of time for the hydrogenation by catalyst 1 is given. This pattern is very similar to that found by Bruner and Bailar (23) in their hydrogenation of soybean oil methylester in 50 % methanol - 50 % benzene solution. I.e., a high selectivity is found for the formation of monoene as long as sufficient unreacted diene is present in the reaction mixture. However, one very serious drawback of this catalyst is the formation of large quantities on trans isomers. The curve representing trans isomers increases almost linearly and follows very closely the curve for the monoene fraction (Fig 4). An alternative way to display the result from this hydrogenation is shown in figure 5. This gives the product pattern at different iodine values and one notices that the triene fraction is completely hydrogenated at an iodine value of 102 while still 37 % of the

diene fraction is present. At the same time the increase in saturates is negligible.

Catalyst 2 and 3, both of which contains only palladium coordinated to two phosphine ligands, have however, no hydrogenation activity at all under the conditions used. This is in line with the behavior of their monomeric analog  $\text{Cl}_2\text{Pd}(\text{P}\phi_3)_2$  which requires higher hydrogen pressure to be active. This difference in reactivity between catalyst 1 on the one hand and catalyst 2 och 3 on the other demonstrate the crucial influence of species II for catalytic activity under low hydrogen pressure. These findings may also explain why the addition of triphenylphosphine inhibits the catalytic activity of this type of catalysts (23): By displacing the pyridine ligand, the triphenylphosphine forms a complex like catalyst 3 with no hydrogenation activity under low hydrogen pressure.

#### Catalyst activation

We have previously noted (24) a temperature dependent activation period for catalysts prepared as catalyst 1. This activation is also coupled with the color change of the catalyst. In order to test the influence of the pyridine ligand in this activation some hydrogenation experiments at different temperatures were done. The result from these experiments are shown in fig. 6.

As can be seen the hydrogenation activity (expressed as decrease in IV) is related to the release of pyridine from the catalyst.



At 100°C the pyridine loss is slow and there is a marked induction period, while at 140°C the loss is faster and the catalyst is active at once.

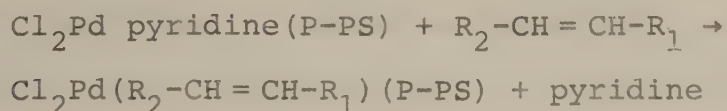
By heating catalyst 1 to 80°C under vacuum (0.01 torr) no pyridine is lost. This probably means that the pyridine in this catalyst, is not bound as a solvate in the axial positions. Instead, as suggested in species II, it is bound as one of the four ligands in the square planar coordinated palladium atom.

One way in which the pyridine might be lost from such a complex is by dimerisation in the matrix.



An increase in temperature will increase the mobility of the polymer network and thus enhance this dimerisation.

The findings of Bailar and Bruner (23) that no benzonitrile was present in the IR-spectra of their catalyst preparations support this suggestion of the formation of the chlorine bridged species. The high phosphorus loading in the polymer used by Bailar et al. (23) and the low complex binding ability for benzonitrile compared to pyridine, can have caused the formation of the bridged complex already at the synthesis stage. Another way in which pyridine might be released is by substitution with an olefine molecule.



Due to the color change noted during the activation, none of the proposed substitution products are, however, likely to be the final stage in the activation (our catalyst is grey-green after hydrogenation,  $\text{Cl}_4\text{Pd}_2(\text{P}\phi_3)_2$  is an orange-red complex and Pd olefine complexes are yellow). Instead one can assume that further reactions cause the formation of the active species. This might well be Pd(0), as small metal particles or as zero valent Pd-phosphine clusters, since a monophosphine complex is probably not as resistant to reduction as a bisphosphine complex. We are at present investigating this and will report the result further on.

#### ACKNOWLEDGMENT

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## References

1. Haag, W.O., and D.D. Whitehurst
  - a) Ger., Offen. 1, 800, 380
  - b) Ger., Offen. 1, 800, 371
  - c) Ger., Offen. 1, 800, 379
2. Michalska, Z.M., and D.E. Webster, Platinum Met. Rev., 18:65 (1974).
3. Bailar, Jr., J.C., Cat. Rev. Scr. Eng. 10:17 (1974).
4. Hartley, F.R., and P.N. Vezey, Adv. Organomet. Chem. 15:189 (1977).
5. Pittman, Jr., C.U., Polymer News 4:5 (1977).
6. Frankel, E.N., and H.J. Dutton, Topics in Lipid Chem. Vol 1, Edited by F.D. Gunstone, Logos Press, London, 1970, p 161.
7. Bailar, Jr., J.C., and H. Itatani, J. Am. Chem. Soc. 89:1592 (1967).
8. Itatani, H., and J.C. Bailar, Jr., Ibid 89:1600 (1967).
9. Bailar, Jr., J.C., JAOCS 47:475 (1970).
10. Bailar, Jr., J.C., Platinum Met. Rev. 15:2 (1971).
11. Frankel, E.N., E.A. Emken, and V.L. Davidson, J. Org. Chem. 30:2739 (1965).
12. Frankel, E.N., E.A. Emken, H.M. Peters, V.L. Davidson, and R.O. Butterfield, Ibid 29:3292 (1964).



13. Frankel, E.N., T.L. Mounts, R.O. Butterfield and H.J. Dutton, *Advan. Chem. Ser.* 70:177 (1968).
14. Frankel, E.N., H.M. Peters, E.P. Jones, and H.J. Dutton, *JAOCS* 41:186 (1964).
15. Frankel, E.N., and F. Little, *Ibid* 46:256 (1969).
16. Frankel, E.N., *Ibid* 47:11 (1970).
17. Frankel, E.N., and R.O. Butterfield, *J. Org. Chem.* 34:3930 (1969).
18. Frankel, E.N., F.L. Thomas, and J.C. Cowan, *JAOCS* 47:497 (1970).
19. Frankel, E.N., and F.L. Thomas, *Ibid* 49:70 (1972).
20. Evans, G.O., C.U. Pittman, Jr., R. McMillan, R.T. Beach, and R. Jones, *J. Organomet. Chem.* 67:295 (1974).
- 21a. Pittman, Jr., C.U., B.T. Kim, and W.M. Douglas, *J. Org. Chem.* 40:590 (1975).
- 21b. Awl, R.A., E.N. Frankel, I.P. Friedrich, and E.H. Pryde, *JAOCS* 55:577 (1978)
22. Bruner, H., and J.C. Bailar, Jr., *Ibid* 49:533 (1972).
23. Bruner, H., and J.C. Bailar, Jr., *Inorg. Chem.* 12:1465 (1973).
24. Andersson, C., and R. Larsson, *Chemica Scripta* 15:45 (1980).
25. Jacobsson, S., W. Clements, H. Hiramoto, and C.U. Pittman, Jr., *J. Mol. Cat.* 1:73 (1975).

26. Pittman, Jr., C.U., and R.M. Hanes, J. Am. Chem. Soc. 98:5402 (1976).
27. Grubbs, R.H., Gibbons, C., Kroll, L.C., W.D. Bonds and C.H. Brubaker, Ibid 95:2373 (1973)
28. Pittman, Jr., C.U., S.K. Wu, and S.E. Jacobson, J. Cat. 44:87 (1976).
29. Chatt, J., and L. M. Venanzi, J. Chem. Soc. (1955) 2787.
30. Kosolapoff, G.M., and L. Maier, Organic Phosphorus Compounds, Vol 1, Wiley, New York, 1972.
31. Method used at the Microanalytical Laboratory, University of Lund, Lund, Sweden.
32. "Official and Tentative Methods of the American Oil Chemists' Society", Vols. 1 & 2, 3rd ed., 1973, AOCS, Champaign, IL, Method Cd 14-61.

Table 1

|                                                    | Differences in catalytic behaviour       |                                                           |
|----------------------------------------------------|------------------------------------------|-----------------------------------------------------------|
|                                                    | $\text{Cl}_2\text{Pd}(\text{P}\phi_3)_2$ | $\text{Cl}_2\text{Pd}$ bound to phosphi-nated polystyrene |
| Hydrogen pressure necessary for activity           | 35 atm                                   | 1 atm                                                     |
| Induction period                                   | none                                     | yes, depending on temperature                             |
| Colour change during hydrogenation                 | remains yellow                           | changes from light yellow to grey-green                   |
| Effect of co-catalyst addition ( $\text{SnCl}_2$ ) | essential for activity                   | makes the catalyst inactive (1 atm $\text{H}_2$ )         |
| Effect of $\text{P}\phi_3$ addition                | (no reports found)                       | makes the catalyst inactive (1 atm $\text{H}_2$ )         |



### Text of figures

- Fig 1 Proposed structures for the two different species formed in the polymer matrix.
- Fig 2 The catalytic hydrogenation apparatus used.
- Fig 3 IR-spectra in the region  $1300 - 1100 \text{ cm}^{-1}$  of 1. Matrix, 2.  $\text{Cl}_2\text{Pd}(\text{P}\emptyset_3)_2$ , 3.  $\text{Cl}_2\text{PdP}\emptyset_3\text{NC}_5\text{H}_5$ , 4. Catalyst 1. 5. Catalyst 3.
- Fig 4 Rate of hydrogenation of soybean oil with catalyst 1 (50.0 gram soybean oil, 1.0 gram catalyst 1,  $140^\circ\text{C}$ , 1 atm  $\text{H}_2$ ).
- Fig 5 % composition versus iodine value in the hydrogenation of soybean oil with catalyst 1 (50.0 gram soybean oil, 1.0 gram catalyst,  $140^\circ\text{C}$ , 1 atm  $\text{H}_2$ ).
- Fig 6 Relation between catalytic activity and the release of pyridine at two different temperatures A  $100^\circ\text{C}$ . B  $140^\circ\text{C}$ , (1 atm  $\text{H}_2$ , 50 gram soybean oil, 1.0 gram catalyst).



FIG.2

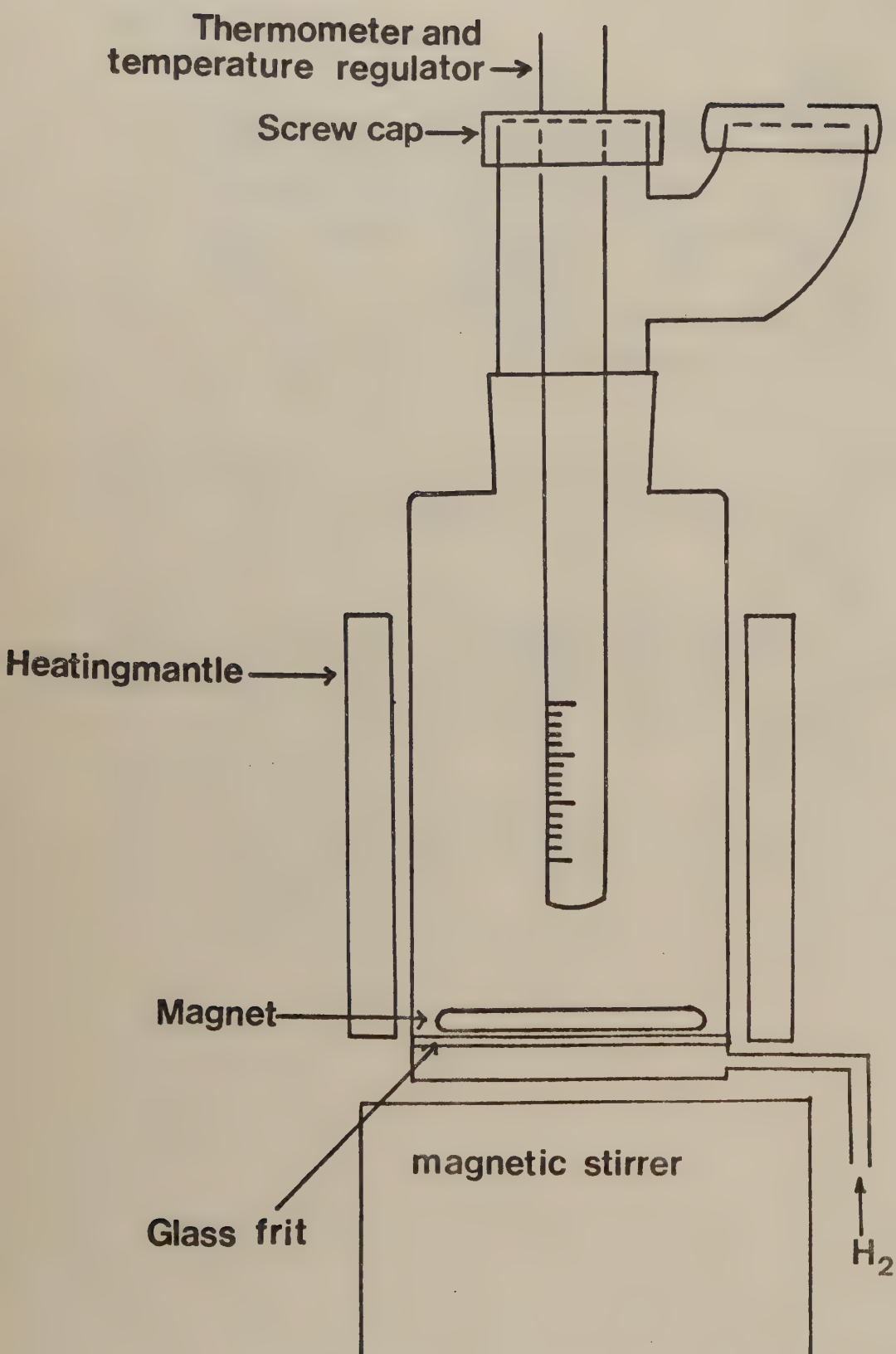




FIG.3

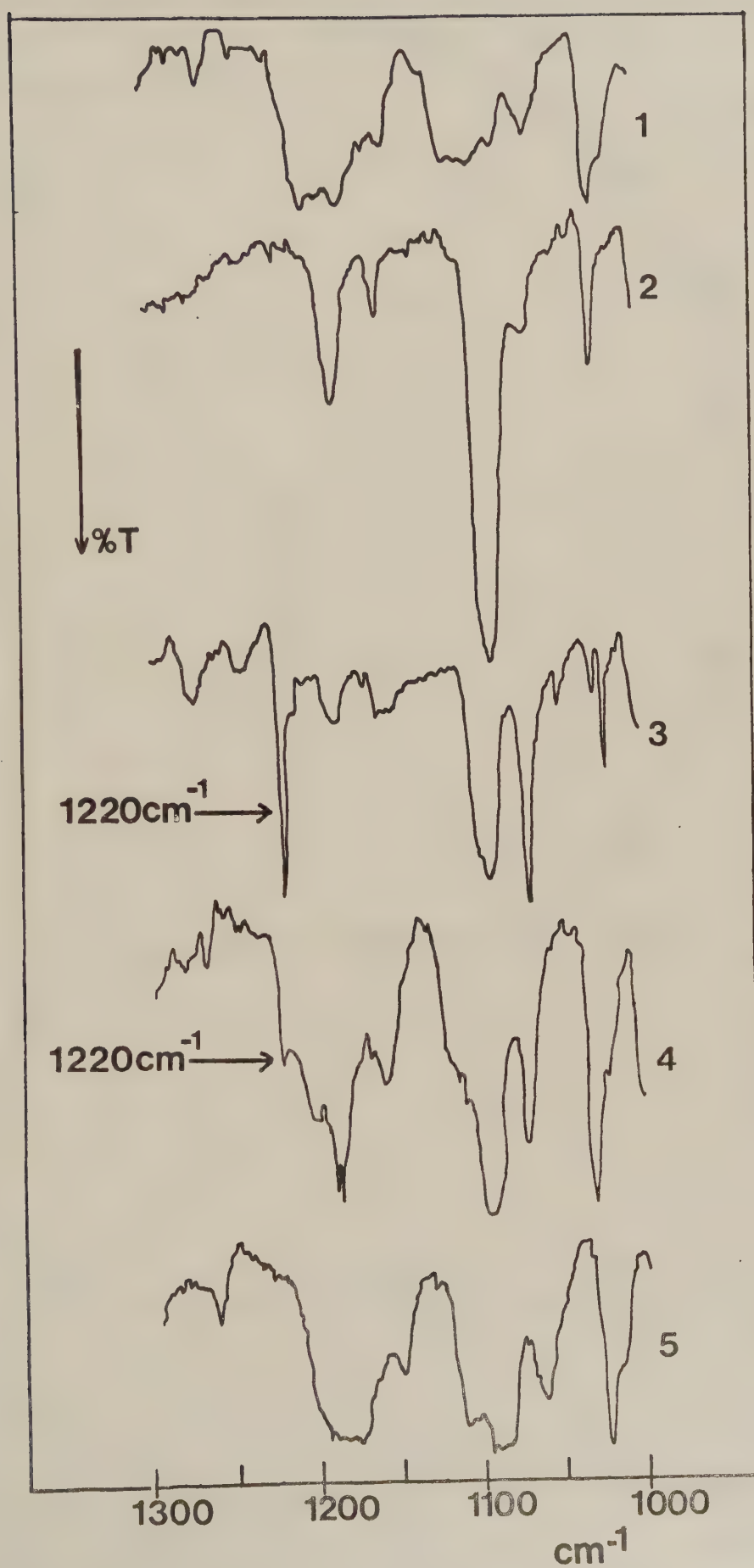


FIG.4

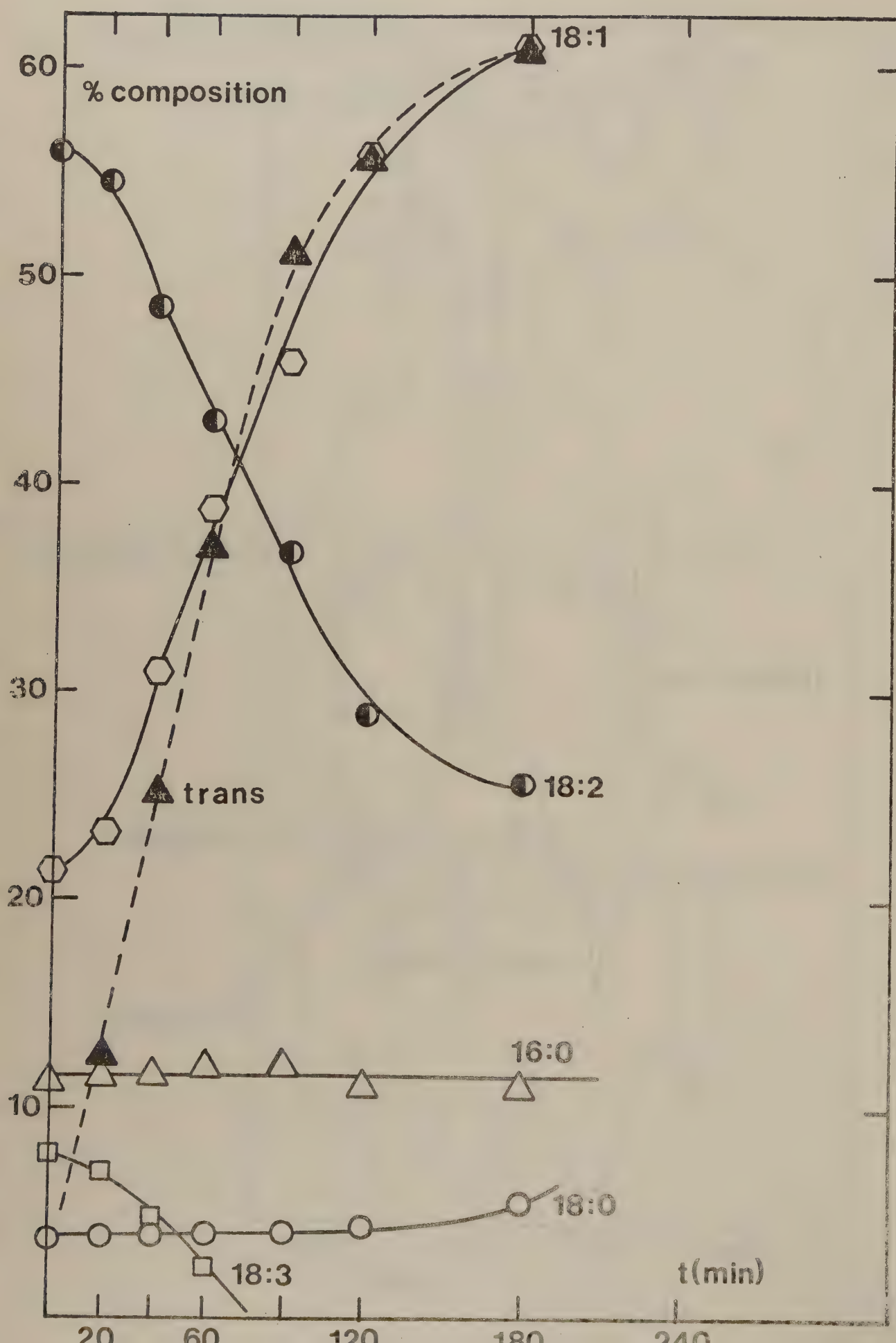


FIG.5

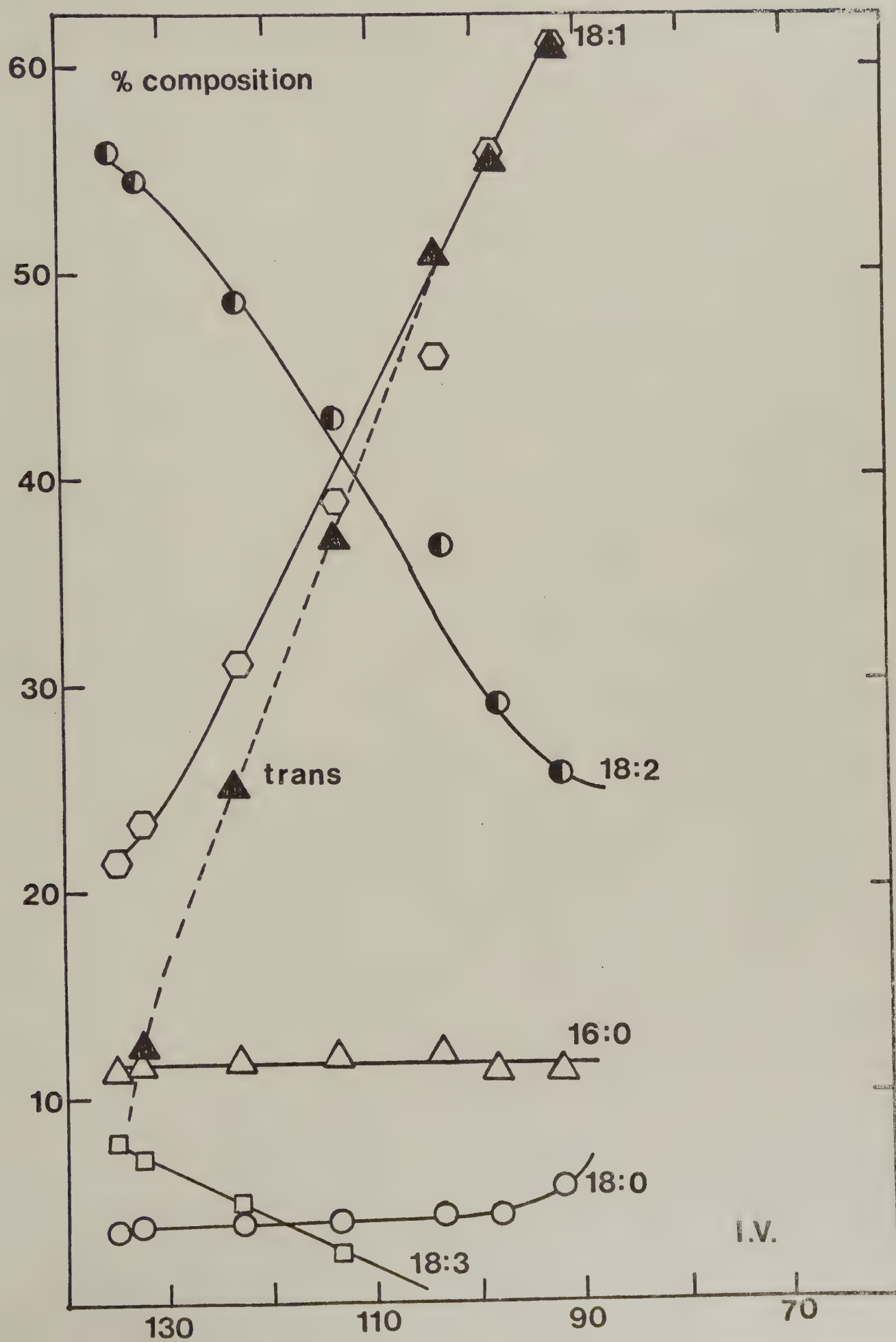
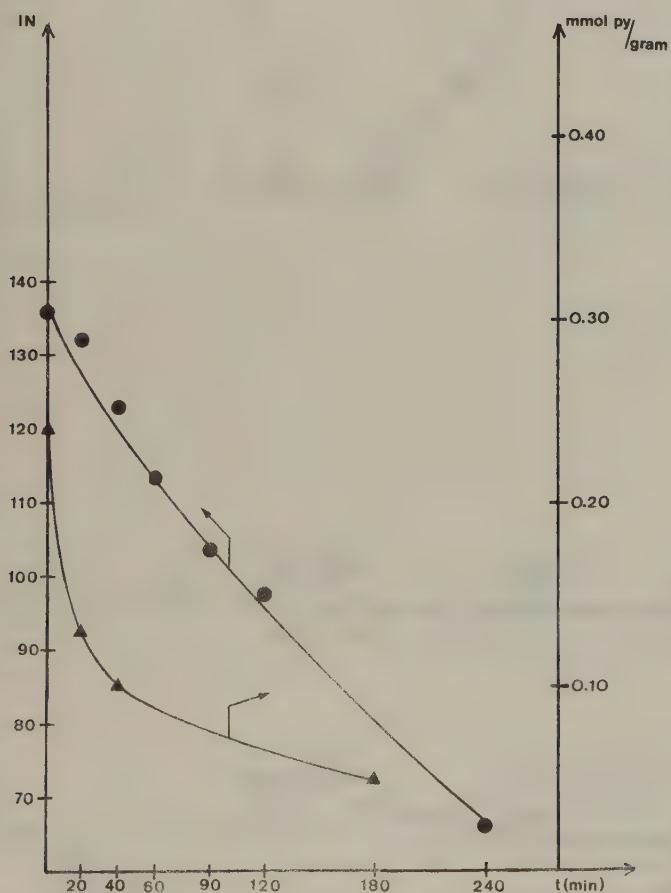
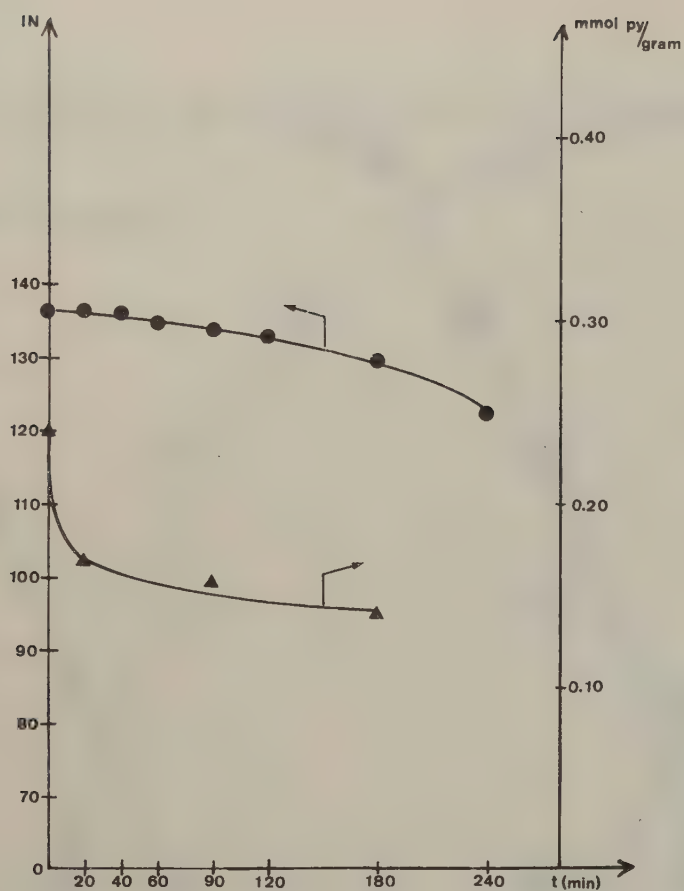




FIG.6



III





SYNTHETIC AND INFRARED STUDIES ON POLYMER  
BOUND PALLADIUM PHOSPHINE COMPLEXES

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## ABSTRACT

The formation of Pd complexes in phosphinated polystyrene resins have been studied. By the use of  $\text{Cl}_2\text{Pd}(\text{pyridine})_2$  as the reacting complex it is shown that depending on polymer properties, such as BET surface area and phosphine content, varying amounts are formed in the resin, of the complex  $\text{Cl}_2\text{Pd pyridine}(\text{P-PS})_1$  together with the complex  $\text{Cl}_2\text{Pd}(\text{P-PS})_2$ . It is found that the monosubstituted complex  $\text{Cl}_2\text{Pd pyridine}(\text{P-PS})$  exists even at formal ratios of  $\text{P/Pd} > 2$ . The presence of "inaccessible phosphine groups" in the resin contributes to this effect. Chemical analysis of the polymers treated with varying amounts of  $\text{Cl}_2\text{Pd}(\text{pyridine})_2$  has made it possible to calculate the "inaccessible phosphine concentration" in the three different polymers used in this study. This quantity is related to the BET surface area. The polymer with low area ( $1.5 \text{ m}^2/\text{g}$ ) has a higher amount of "inaccessible phosphine groups" than the polymer with the higher surface area ( $53.5 \text{ m}^2/\text{g}$ ).

With  $\text{Cl}_2\text{Pd}(\text{benzonitrile})_2$ , as the reacting complex, no analogous mixed complex is found in the resin. This system was studied by infrared spectroscopy in the M-Cl stretching region and in the spectral range of characteristic vibrations of some extra ligands (CO, 4-cyanopyridine) that were combined with the system. From these measurements we have concluded that complexes of the type  $(\text{PS-P})-(\text{PdCl}_2)_n-(\text{P-PS})$  where  $n \geq 3$  are formed in the resin together with the bisphosphine complex.

The rôle of the species  $\text{Cl}_2\text{Pd}(\text{pyridine}(\text{P-PS}))$  and  $(\text{PS-P})-(\text{PdCl}_2)_n-(\text{P-PS})$  in catalytic applications of the resins are briefly discussed.

## INTRODUCTION

### General review

Since the development of the technique of attaching soluble coordination catalysts to polymeric supports, this has become an active field of research. Most papers published in this area have, however, mainly dealt with catalytic reactions i.e. studies on activity and selectivity. Studies with the primary interest to determine the constitution of the catalysts themselves have been rather rare. As many of the systems that have been used, behave similarly to their homogeneous counterparts, and as the latter ones often are well characterised, further studies have not seemed to be necessary. The assumption has been made that in both cases the same active species are operating. In those cases where the homogeneous and the heterogeneous systems give different results, and consequently a need for a deeper understanding exists, the investigator is often faced with major difficulties. The advantages of heterogenized systems such as easier handling and more efficient product separation are always accompanied by the disadvantage of more limited means by which structural information can be obtained. This is the same kind of problem as the one met in traditional heterogeneous catalysis.

Grubbs and Sweet (1) have used microprobe analysis to determine the distribution of metal and ligand atoms inside the polymer beads. Although important information is gained in this way, it gives no information of the metal-ligand arrangement in the polymer. Phosphorus ( $^{31}\text{P}$ ) NMR has been used to study metal binding (Rh) to phosphinated polystyrene (2). By this technique the amount of phosphine complexed as a function of the amount of metal added could be determined. Very valuable information on

molecular structure was actually gained in this study (2), namely that a change from a trisphosphine complex to a bisphosphine complex took place on increased metal loading.

Photoacoustic spectroscopy (PAS) is a new technique that can be applied to materials unsuitable for study by conventional optical methods. PAS has been used to study and characterize the species formed on irradiation of  $W(CO)_6$  in the presence of polyvinylpyridine (3). Yet another technique that has been successfully applied to determine the composition of heterogenized complexes is EPR. Using the method of paramagnetic probes Russian scientists (4) were able to determine the distribution of complexes of palladium on silica.

Infrared spectroscopy is also a method that has been used for studying the metal ligand arrangement in complexes and surface compounds. Especially one can get much information from the frequency and absorption intensity of adsorbed carbon monoxide. In this way CO can be regarded as an IR probe for surface chemistry (5, 6, 7).

#### Palladium-phosphine polystyrene systems

IR spectroscopy together with chemical analysis provided the information needed to determine the complex formed on reacting  $Cl_2Pd(pyridine)_2$  with phosphinated polystyrene (8).

Palladium(II) chloride bound to phosphinated polystyrene is a system where major differences between the homogeneous and the heterogeneous system have been found (9, 10, 11, 12). It is also a system where somewhat deviating suggestions have been made as to what complex actually is formed in the polymer. E.g. in the work by Bruner and Bailar (9, 10) the polymer catalyst was synthesised by reacting  $Cl_2Pd(benzonitrile)_2$  with the



polymeric ligand and these authors suggest the formation of a bisphosphine complex in the matrix. Terasawa et al. (12) synthesised their catalyst by reacting the polymeric ligand with  $\text{PdCl}_2$ . From analytical, IR and XPS results they suggest that the coordinatively unsaturated complex  $\text{Cl}_2\text{Pd}(\text{P-PS})$  is formed. (P-PS is the polymeric ligand.) This latter complex is somewhat similar to what we have found (8): When  $\text{Cl}_2\text{Pd}(\text{pyridine})_2$  was reacted with phosphinated polystyrene, only one phosphorus atom in the polymer was coordinated for each metal atom, the other coordination site was occupied by a pyridine ligand ( $\text{Cl}_2\text{Pd pyridine (P-PS)}$ ).

The  $\text{X}_2\text{Pd}(\text{phosphine})_2$  type of catalyst has interesting applications as a hydrogenation catalyst. Meaningful discussion on its reactions can not be carried out however, if the constitution of the catalyst is unknown. We have therefore continued our investigations on such systems, started in ref. (8). In doing this we have synthesised a number of catalysts using different matrixes and various preparative methods, and used IR spectroscopy with several probes to elucidate the structure of the complexes formed in the matrix.

## EXPERIMENTAL

Infrared spectra were measured with a Perkin Elmer 580B spectrometer equipped with PE Data Station. The catalysts were sampled as KBr or polyethylene pellet suspensions except for the CO treated catalysts which were examined as Nujol mulls.

### Materials

All chemicals and solvents used were of analytical grade. KBr and polyethylene used for the IR measurements were spectroscopi-

cally pure. Chloromethylated polystyrene was purchased from Merck (Merrifield Harz art.no. 805064) and from Pierce (No. 24600). Dichlorobisbenzonitrile palladium(II)  $\text{Cl}_2\text{Pd}(\text{benzonitrile})_2$  (13) and dichlorobispyridine palladium(II)  $\text{Cl}_2\text{Pd}(\text{pyridine})_2$  (8) were prepared by literature methods. p-styrenediphenylphosphine  $\text{CH}_2 = \text{CH}-\text{C}_6\text{H}_4-\text{P}(\text{C}_6\text{H}_5)_2$  was prepared according to the method given by Rabinowitz and Marcus (14). Lithium diphenylphosphine  $\text{Li P}(\text{C}_6\text{H}_5)_2$  was generated from Li and  $\text{P}(\text{C}_6\text{H}_5)_3$  (15).

#### Preparation of phosphinated polymers

The chloromethylated polystyrenes (Merck, Pierce) were phosphinated by reacting the polymers with  $\text{Li P}(\text{C}_6\text{H}_5)_2$  in dry THF under nitrogen (4). The styrene p-styrenediphenylphosphine co-polymer was prepared by rapid stirring of a solution of 12.5 ml styrene, 0.5 ml divinylbenzene solution (50%) and 8.0 gram of p-styrene-diphenylphosphine in water suspension at  $70^\circ\text{C}$  over night. 250 mg of azo-iso butyronitrile was used as initiator.

Work up procedures for all polymers were the same as those given earlier (8). Phosphorus analysis are given in Table 1.

#### Preparation of polymer-bound Palladium complexes

These were all done by the same general procedure. E.g. calculated amount of palladium complex was dissolved in  $\text{CH}_2\text{Cl}_2$  under nitrogen. Calculated amount of the phosphinated polymer was then added to this solution. The mixture was shaken for 24 hours. The polymer was recovered by filtration and washed. It was then extracted with  $\text{CH}_2\text{Cl}_2$  for 24 hours in a Soxhlet apparatus.

The methods of analysis have been given before (8). Data for all the preparations are given in Table 2.

## Reactions with CO

Those samples which were selected for CO treatment were first finely ground and then placed in a glass vessel with a sidearm equipped with a membrane. The vessel was first evacuated to ca 0.1 torr and then filled with dried CO to 600 torr. After 12 hours contact time Nujol was injected through the membrane and the flask was gently shaken in order to let the Nujol carefully wet the polymer. The later procedure is important, as the CO-complex formed is very moisture sensitive. Without protection the polymer darkens in a few minutes. If, however, the polymer is protected from moisture as described the polymer can be easily handled and IR-spectra taken. The reason for this darkening of the CO-Pd polymer in moist air will be discussed together with the IR spectra of the CO complexes (p 13 ).

## RESULTS AND DISCUSSION

Table 1 gives the data for the three different polymers that we have used in this study. They are all of the swellable, microporous type, although differentiating in surface area rather much.

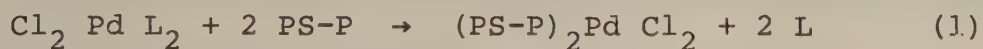
The phosphorus content in Table 1 represents total phosphorus. Some of the phosphines in the polymer will, however, presumably be located so that they are not easily accessible. The amount of the phosphines that can be used for metal binding depends on polymer properties such as porosity.

The method of preparation can also influence the amount of accessible phosphorus. An example from the chemistry of Rh can help to illustrate this, e.g. if  $\text{ClRh}[\text{P}(\text{C}_6\text{H}_5)_3]_3$  is reacted with the phosphinated polystyrene matrix, it needs only one phosphine



in the polymer to form the desired Wilkinson analogue  $\text{ClRh}[\text{P}(\text{C}_6\text{H}_5)_3]_2$  P-PS. In this way also isolated phosphines in the matrix can be used if there is enough space to accomodate the bulky complex at all. On the other hand if the synthesis is done by reacting  $[\text{RhCl}(\text{C}_6\text{H}_5)_3]_2$  with the phosphinated polystyrene three phosphines in the matrix are needed to form the desired  $\text{ClRh}(\text{P-PS})_3$  complex. In this way only those phosphine groups that are close together or which by chain deformation can be brought close together, can be used. The amount of accessible phosphorus is accordingly in a way determined by the type of reaction.

In the present study we have touched upon these problems as we have used different polymers and different preparative routes. The two methods of preparation we have used are both based on ligand substitution reactions, that is to say substitution of a less strongly coordinating ligand (in this case a N-donor ligand such as pyridine or benzonitrile) by the polymeric phosphine. Both methods of preparation require that two P-groups must be supplied from the polymer to form the complex (eq. 1)



(L = pyridine, or benzonitrile)

This in turn requires that the phosphines are, or can be, arranged so that a bisphosphine complex can be formed. We have previously shown (8) that, when a phosphinated polystyrene with 1.8 % P and a Pd/P ratio of 1:2 was used, the substitution is not complete but that a mixed complex  $\text{Cl}_2\text{Pd}(\text{pyridine})(\text{P-PS})$  is the dominating species in the matrix. As the pyridine ligand in the matrix is easily detectable by IR spectroscopy or by analytical methods, the synthesis from  $\text{Cl}_2\text{Pd}(\text{pyridine})_2$  is one



way in which it is possible to get an idea about the most favourable conditions for formation of the bisphosphine complex.

#### Synthesis from $\text{Cl}_2\text{Pd}(\text{pyridine})_2$ —

By reacting the three different polymers with different amount of  $\text{Cl}_2\text{Pd}(\text{pyridine})_2$  a set of preparations, with different P/Pd ratios were obtained. The analytical results for these preparations are given in Table 2. Although the variation in the total phosphorous content between the various polymers is relatively small a difference in complex formation can be seen. For instance polymer PII, with the lowest phosphorous content gives the formation of the mixed  $\text{Cl}_2\text{Pd}(\text{pyridine})(\text{P-PS})$  complex in spite of that the ratio P/Pd used is such (2.3:1) that the bisphosphine complex might have been formed. Indeed if the polymer PII is treated with an even larger quantity of the metal complex (P:Pd = 1.1:1), the amount of metal incorporated remains the same. This polymer reaches a state of saturation even though not all phosphorus is used (P/Pd = 4.7). It follows that the polymer PII holds a relatively large amount of not accessible phosphine groups. In a following section (page 49) we have discussed the concept of "inaccessible phosphine groups" and also showed how this number can be calculated. For the polymer PII the relative amount of not accessible phosphine groups ( $C_{\text{P}_{\text{inacc.}}} / C_{\text{P}_{\text{tot.}}}$ ) is very high (74%) (Table 1), and this polymer reacts quite differently compared to the others.

Polymers PI and PIII which have a much lower but about the same relative amount of inaccessible phosphine groups (~ 30%, Table 1) reacts both according to the same pattern. That is, treatment of the polymers at high P/Pd ratios is accompanied by a formation of the bisphosphine complex  $\text{Cl}_2\text{Pd}(\text{P-PS})_2$  as the

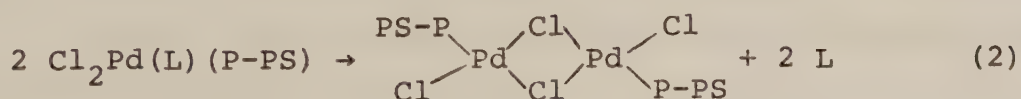
main species (see preparation 011, 037, 038). On synthesis at P/Pd ratios close to 2 the formation of the mixed complex  $\text{Cl}_2\text{Pd}(\text{pyridine})(\text{P-PS})$  is fully noticable (preparation 039). Preparations carried out with lower P/Pd ratios (preparations 012, 019, 040) result in a nearly complete formation of the mixed complex. From these observations one can rather safely state that the amount of accessible phosphine groups is one of the factors that determines the complex formation inside the polymers. Consequently it is important to be able to determine this quantity.

In the formation of the bisphosphine complex two phosphine groups in close proximity are needed. This can be achieved in two ways. Either by increasing the phosphorus content and thereby decreasing the distance between the phosphine groups, or by changing polymer properties such as chain deformation ability, making the phosphine groups more mobile. The three polymers used in this study, have however the same degree of crosslinking (2%), and thus any great variation in phosphine mobility should not be expected. However, besides the degree of crosslinking one other effect that must be recognized in connection with phosphine mobility is that metal coordination can create a more rigid polymer. Such effects have been noted before (16). The observation that PI and PII, which both at low metal loadings form mainly the bisphosphine complex, change to form also the monophosphine complex might be due to such an effect. The energy needed to change the chain conformation so that the bisphosphine complex can be formed increases for each metal atom coordinated in that case.

### Synthesis from $\text{Cl}_2\text{Pd}(\text{benzonitrile})_2$

Knowing how the polymer PI reacted on increased metal loading in the formation of the complex  $\text{Cl}_2\text{Pd}(\text{pyridine})(\text{P-PS})$ , we found it interesting to study the same polymer reacting with  $\text{Cl}_2\text{Pd}(\text{benzonitrile})_2$ . Also for such a preparative route Pittman found that P/Pd ratios less than two can be achieved (17). No sign of benzonitrile present in the resin after reaction was found in our preparations (Table 2). Neither have other studies (10, 11) showed the presence of benzonitrile in the polymers.

The first step in the substitution in the pyridine case as well as in the benzonitrile one is most likely the same. This means that even in the last case should a mixed complex  $\text{Cl}_2\text{Pd}(\text{benzonitrile})\text{P-PS}$  be formed. Because of the low complex-binding ability of benzonitrile combined with the high trans-effect of the phosphine ligands, this is probably a very unstable complex. One can therefore assume that such a complex will react further. Different possible routes for further reactions exist, for example the formation of a coordinatively unsaturated complex by release of the benzonitrile ligand. However, this is not a very likely reaction since it is well known that such coordinatively unsaturated complexes are mostly very reactive. A chemically more attractive way for further reactions from the unstable  $\text{Cl}_2\text{Pd}(\text{benzonitrile})(\text{P-PS})$  complex is a dimerisation (eq. 2).



(L = benzonitrile)



From the analytical data in Table 2 no information, as to what species is formed on high metal loading can be obtained. (At first sight, this is true. In a following section we will see that analytical data are of value even in this respect.) Analytical data does, however, inform us that a bisphosphine complex can not be the only species in the resin at high metal loading since a P/Pd ratio less than two can be obtained. It does also inform us that if polymer PI is treated with either  $\text{Cl}_2\text{Pd}(\text{pyridine})_2$  or  $\text{Cl}_2\text{Pd}(\text{benzonitrile})_2$  in a P/Pd ratio of 1, the benzonitrile case gives a much higher metal incorporation (6.6 % Pd compared to 4.2 % Pd for the pyridine case). This must mean either that more phosphorus is accessible in the benzonitrile case, or that each accessible phosphorus atom is shared with more than one palladium atom.

#### Infrared studies

The coordinatively unsaturated complex as well as the bridged complex can be expected to behave chemically very similar. On treatment with a Lewis base L they will most likely give the same product according to scheme 1. A suitable Lewis base L, i.e. one that does not destroy the bisphosphine complexes, easy to detect, e.g. by infrared spectroscopy, should therefore make it possible to show the existens of such species.

#### 4-cyanopyridine

For this purpose we have reacted preparation 036 with 4-cyanopyridine. This choice was made for two reasons. Firstly,  $\text{Cl}_2\text{Pd}(\text{pyridine})(\text{P-PS})$  has been shown to be stable in the resin. Secondly, the cyano group on the pyridine ring permits an easy identification by infrared spectroscopy to be done, as the



$C \equiv N$  stretching absorption is strong and appears in a spectral region where resin absorption does not disturb.

On reacting preparation 036 with 4-cyanopyridine (Pd:4-cyanopyridine = 1:1) in  $CH_2Cl_2$  the original deep orange colour of the resin changed to light yellow and palladium was extracted. ( $Cl_2Pd(4\text{-cyanopyridine})_2$  could be identified in the solution.) Extraction of palladium down to a level comparable to the metal content of preparation 040 could perhaps be expected as the maximum possible content of  $Cl_2Pd$  pyridine(P-PS) seems to be of that order. Much more was, however, extracted judged from the amount of  $Cl_2Pd(4\text{-cyanopyridine})_2$  formed although no quantitative measurements were done. This extraction of palladium does not make the results obtained with 4-cyanopyridine as conclusive as we hoped them to be. Taken together with other results of this study, however, even this extraction can be explained.

In the infrared spectra of the 4-cyanopyridine-treated polymers a very weak signal at  $2239\text{ cm}^{-1}$  was present. On comparison with the spectra of the complex derived from reaction of  $Cl_4Pd_2(P(C_6H_5)_3)_2$  with 4-cyanopyridine giving  $Cl_2Pd P(C_6H_5)_3^-$  (4-cyano)-pyridine this can be assigned to  $C \equiv N$  stretch in  $Cl_2Pd(4\text{-cyanopyridine})(P\text{-PS})$ .

Infrared spectra thus show that the expected products is formed (scheme 1) but to a rather small extent.

#### Carbon monoxide

Another Lewis base useful as an infrared probe is CO. When preparation 036 suspended in solvents like acetone, ethanol or  $CH_2Cl_2$  was treated with CO, the polymer darkened and nothing but black polymers could be recovered showing no sign of

carbonyl bands in their infrared spectra. We therefore changed to perform the CO treatment in the solid state under such conditions that moisture was carefully excluded. Using the method outlined in the experimental section the spectrum A given in Figure 1 was obtained after 15 hours CO treatment. This spectrum shows two bands in the CO stretching region. One band positioned at  $2125\text{ cm}^{-1}$  and another at  $1925\text{ cm}^{-1}$  both with about equal intensity. If the Nujol mull was left in air the spectrum gradually changed and spectrum B was obtained. The peak at  $2125\text{ cm}^{-1}$  in A has disappeared and a new peak at  $1970\text{ cm}^{-1}$  is present instead. This new peak is of lower intensity than the one at  $2125\text{ cm}^{-1}$ . It is also worth noting that the peak at  $1925\text{ cm}^{-1}$  is unchanged by this treatment. However, on addition of a very moist solvent, like dioxan with a small amount of water added, the polymer becomes black. The most likely explanation to this latter reaction is a reduction of the Pd-CO complex or complexes in the resin to form Pd metal. This is also evident from the infrared spectrum as it shows no carbonyl bands after treatment of the Nujol mull with moist solvents (spectrum C).

Numerous workers have investigated the reaction of CO with Pd halides (18, 19, 20, 21, 22), with varying formulations of the complex formed. More recent studies (23, 24) have, however, established that CO reacts with Pd halides to form the complex  $(\text{PdClCO})_n$  with alternating CO and X bridges. This complex has the CO-stretching mode about  $1978\text{ cm}^{-1}$ . It can be isolated as a yellow (or yellowgreen) solid, and it is unstable to heat and moisture. Goggin and Mink in their study (24) reacted  $\text{PdCl}_4^{2-}$  with CO and initially observed a band at  $2132\text{ cm}^{-1}$  corresponding to the ion  $[\text{Cl}_3\text{PdCO}]^-$ . On prolonged treatment

this band decreased and new bands at  $1966\text{ cm}^{-1}$  and  $1904\text{ cm}^{-1}$  (s) appeared. After reaction a solid phase of composition  $\text{Pr}_4^{\text{n}}\text{N}[\text{PdCl}_2\text{CO}]$  could be isolated on addition of  $\text{Pr}_4^{\text{n}}\text{NCl}$ . The anion  $\text{PdCl}_2\text{CO}^-$  ( $\nu\text{C}\equiv\text{O}\ 1915\text{ cm}^{-1}$ ) was formed on reaction of CsCl with  $(\text{PdClCO})_n$  (23) and  $\text{R}_4\text{N}(\text{PdCl}_2\text{CO})$  salts ( $\nu\text{C}\equiv\text{O}\ 1963\text{ vw}$ ,  $1905\text{ s cm}^{-1}$ ) could be prepared by reacting  $(\text{PdClCO})_n$  with the appropriate tetraalkylammoniumchloride. From this collected evidence we conclude that CO reacts with  $\text{PdCl}_4^{2-}$  or  $\text{PdCl}_2$  first to form the ion  $\text{PdCl}_3\text{CO}^-$  ( $\nu\text{CO}\ 2132\text{ cm}^{-1}$ ) or  $\text{PdCl}_2\text{CO}$ . On further reaction involving reduction  $(\text{PdClCO})_n$  ( $\nu\text{C}\equiv\text{O}\ 1978\text{ cm}^{-1}$ ) is formed which on treatment with a chloride containing salts gives the ion  $\text{PdCl}_2\text{CO}^-$  ( $\nu\text{C}\equiv\text{O}$  around  $1910\text{ cm}^{-1}$ ). Part of this pattern i.e. the formation of a carbonyl complex absorbing at  $2125\text{ cm}^{-1}$  which then reacts to give a peak at  $1970\text{ cm}^{-1}$ , can also be observed in our spectra (A, B). Now the question arises: Where does then  $\text{PdCl}_4^{2-}$  or  $\text{PdCl}_2$  come from? As stated in the beginning of this section we were suspecting the existence of either the coordinatively unsaturated complex PS-P  $\text{PdCl}_2$  or the bridged complex  $(\text{PS-P})\text{Pd}_2\text{Cl}_4$ . None of these structures can, to our opinion explain our CO spectra. If, however, the bridged complex is extended to contain more than two palladium atoms we arrive at a structure containing  $\text{PdCl}_2$  units. We therefore suggest that at high Pd loadings the polymer contains species of the type  $(\text{PS-P}) - (\text{PdCl}_2)_n - (\text{P-PS})$  with bridging Cl atoms.

On reaction with CO the chloride bridges are cleaved and  $\text{PdCl}_2\text{CO}$  is formed from the  $\text{PdCl}_2$  units in the chain, giving rise to the band at  $2125\text{ cm}^{-1}$ . The band we observe at  $1925\text{ cm}^{-1}$  is then arising from CO bonded to the two end groups. The pos-



ition of this band corresponds to what is frequently observed for bridged CO in Pd(I) complexes (e.g.  $\nu$  C $\equiv$ O 1948 for CO trans to PhCN in  $(\text{PdClCO})_3\text{PhCN}$  (24)). The assumption can therefore be made that Pd in this complex is reduced to Pd(I) and that the two end groups are bridged by CO to form a dimer. It is possible that CO acts as the reducing agent forming e.g. phosgene.

By keeping the Nujol mull in open air slow diffusion of moisture is a possible reaction. The changes in the spectra that we have observed (compare A and B) can therefore depend on a limited reduction of the  $\text{PdCl}_2\text{CO}$  complex in the matrix to form the Pd(I) complex  $(\text{PdClCO})_n$  with CO adsorption at  $1970\text{ cm}^{-1}$ .

On treatment with larger amounts of water both CO complexes are reduced to Pd metal as judged by the colour change and disappearance of the CO peaks in the spectrum. A complete scheme for the reactions discussed are given in Figure 2. This scheme must not, however, necessarily involve the suggested long chained bridged species. The same reaction scheme can also be applied to a case where excess palladium (compared to a stoichiometric ratio P/Pd (2) is  $\text{PdCl}_2$  deposited as such in the matrix, in addition to the coordinatively unsaturated species. But in such a case an explanation of the benzonitrile release and the  $\text{PdCl}_2$  deposition is necessary.

It must be stressed that the bridged species  $\text{Cl}_4\text{Pd}_2(\text{P-PS})_2$  formulated above does not give rise to the CO spectra that we have observed. This can be deduced from the fact that  $\text{Cl}_4\text{Pd}_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$  does not react with CO although the Pt analogue reacts and forms the complex  $\text{P}(\text{C}_6\text{H}_5)_3\text{PtCl}_2\text{CO}$  (25). The same result concerning  $\text{Cl}_4\text{Pd}_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$  was also noted in



another study published during the course of this work (26). These authors have prepared similar polymer-bound Pd-complexes and reacted them with CO. They report CO stretching frequencies in the region 1964-1947  $\text{cm}^{-1}$  for polystyrene resins and around 1945  $\text{cm}^{-1}$  for vinylalcohol resins and suggest that  $\text{Cl}_2\text{Pd}(\text{CO})\text{P-PS}$  species are formed. The rather low frequencies reported does, however, point to the fact that even in this case bridged Pd (I) complexes have probably been formed in the resins.

We can now return to the results obtained on treatment with 4-cyanopyridine. The extraction by 4-cyanopyridine, of quite a large portion of the palladium in the resin, is puzzling if only  $\text{Cl}_4\text{Pd}_2(\text{P-PS})_2$  or  $\text{Cl}_2\text{Pd}(\text{P-PS})$  is present in the resin. Taking into account the presence of  $(\text{PS-P})-(\text{PdCl}_2)_n-(\text{P-PS})$  it is easy to imagine how this extraction occurs. Attack by the 4-cyanopyridine on the chloride bridges causes the interjacent  $\text{PdCl}_2$  units to be released by the formation of (4-cyanopyridine) $_2\text{PdCl}_2$ . Left in the polymer of the palladium originally present, is then as  $\text{Cl}_2\text{Pd}(4\text{-cyanopyridine})(\text{P-PS})$  only a minor part.

#### Metal-halide vibrations

Further support for the formation of larger Pd aggregates can be derived from infrared spectra in the metal-chloride stretching region. Stretching frequencies for a large number of different palladium chloride complexes with reliable assignments can be found in the literature (25). Different problems can, however, arise if this method is applied to metal-chloride complexes in polymeric resins. Firstly, as this type of complexes often are prepared in such a way that they are present in low concentrations in the matrix, the weak signals corre-

sponding to M-Cl can be hard to detect and distinguish. Secondly, no study of intra ligand deformation modes in polymeric phosphine ligands have to our knowledge been done. These problems can, however, be overcome. By the use of modern infrared spectrometers equipped, with data handling facilities, spectra can be expanded with retained signal to noise ratio. If necessary background (matrix alone) spectrum can be subtracted and so on. We have used this technique to study the complexes prepared from polymer PI in the region 400-180  $\text{cm}^{-1}$ . Figure 3 shows a typical spectrum for the complexes prepared from  $\text{Cl}_2\text{Pd}(\text{pyridine})_2$  with the main peak at 353  $\text{cm}^{-1}$ . This corresponds to a peak present in trans  $\text{Cl}_2\text{PdL}_2$  complexes ranging from 357 to 353 depending on phosphine. This peak is also found in  $\text{Pd}_2\text{X}_4(\text{PR}_3)_2$  complexes (27) and is assigned to terminal Pd-X stretching. The small peaks at 295  $\text{cm}^{-1}$  and 265  $\text{cm}^{-1}$  are present in all spectra with an intensity roughly independent of metal content in the polymer. This fact indicates that they are intra ligand vibrations and not  $\text{M} \begin{array}{c} \text{Cl} \\ \diagup \quad \diagdown \\ \text{Cl} \end{array} \text{M}$  skeletal vibrations that are found at 297 and 260  $\text{cm}^{-1}$ , e.g. in  $\text{Cl}_4\text{Pd}_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$ . Another reason for this interpretation arises from the intensity ratio found for these two peaks. In all our spectra these are present in about equal intensity while in  $\text{Cl}_4\text{Pd}(\text{PR}_3)_2$  complexes a ratio  $A_{260}/A_{297}$  of 2 has been found (27). The peak present at 220  $\text{cm}^{-1}$  in our spectra is, however, depending on the metal loading of the polymer and this fact indicates that it can be assigned to some kind of M-Cl vibration, possibly a combination mode of a bending mode and a M-P mode. As this band is not present for the complexes prepared from  $\text{Cl}_2\text{Pd}(\text{benzo-}$

nitrile)<sub>2</sub>, however, an alternative explanation is that this band is due to coordinated pyridine. If we now turn to the spectra obtained with the complexes prepared from Cl<sub>2</sub>Pd(benzonitrile)<sub>2</sub> (figure 4) the same three peaks as in figure 3 are present at low Pd loading (spectrum A) with the peak at 353 cm<sup>-1</sup> by far the most intense. Increasing the Pd loading (spectrum B) does not alter this situation much, but at the highest Pd loading (spectrum C) drastic changes occur. Firstly the peak at ~353 cm<sup>-1</sup> is broader and on 5 times abscissa expansion (spectrum E) it is clear that this peak contains, in fact, two peaks, one at 353 cm<sup>-1</sup> and the other at 340 cm<sup>-1</sup>. The one at 340 cm<sup>-1</sup> with a slightly lower intensity. Secondly the intensity ratio of the two peaks at 295 cm<sup>-1</sup> and 258 cm<sup>-1</sup> have changed, so that now the peak at low wave-number is more intense (ratio about 2:1). The new peak appearing at 340 cm<sup>-1</sup> is at the same position as the stretching vibration of the Pd-Cl bridges in solid PdCl<sub>2</sub> (28). PdCl<sub>2</sub> in the solid state consists of infinite chains of square-planer PdCl<sub>4</sub> units (29). We therefore conclude that this spectrum is consistent with the suggestion made earlier, that this polymer contains long chains of palladium atoms with chloride bridges. The changed intensity ratio for the two peaks at lower wave-number, might perhaps mean that even dimers are present in the polymer. This can, however, also be due to the long chain species present.

A careful examination of the spectra obtained with preparation 035 reveals that also this contains the peak at 340 cm<sup>-1</sup> as a very weak shoulder (spectrum D). This can be seen more clearly if the difference spectrum between pre-



paration 035-039 is formed. Such a spectrum is shown in figure 5.

Taken together, the studies we have undertaken on the complexes prepared from  $\text{Cl}_2\text{Pd}$  benzonitrile show clearly that in this case, the polymer contains long chained Pd species at high metal loading. We therefore suggest that the different reactions possible using different synthetic routes can be summarized as is done in scheme 2, with no implications to the actual mechanism of the reaction.

#### Calculations on the analytical data

Let us now once more turn to the interpretation of the analytical data left open in the introductory paragraph. Admittedly, we present a rather limited number of data but at least for two of the investigated resins, PI and PIII treated with the pyridine complex, we have a possibility of interpretation. This interpretation will start from some concepts already introduced in the discussion above:

- 1) The Pd complexes that are formed have a coordination number of four.
- 2) There is only a certain part of the phosphine groups in the polymer that is accessible for coordination. Several reasons for this inaccessibility may exist, one of them is most certainly the blocking by neighbouring groups from the polymer units. As said above (p. 10) the number of phosphines blocked may very well vary with degree of metal loading of the resin because of a change in conformation and superstructure. For the present analysis we neglect this possibility, however, and consider a certain concentration of inaccessible phosphine groups,  $C_p'$ , as constant for one and

the same preparation of polymer.

3) The palladium(II) phosphine complexes are thermodynamically very stable. This means that the concentration of phosphine groups necessary to drive the equilibrium of the formation reaction to species of maximum coordination number is very small. Indeed we will neglect this quantity in comparison with other terms. (This does not mean that there cannot exist 'free' phosphine groups. If the metal loading of the resin is so low that the maximum coordination number is reached without consuming all available groups, some must quite simply be left over.)

We further note that we have three different analytical quantities to deal with: The total phosphine concentration  $C_P$ ; the total metal concentration  $C_{Pd}$  and the concentration of coordinated pyridine  $C_{py}$ .

Assuming that all metal atoms are kept in the resin because they are coordinated to one or two phosphines we can write the following mass balance equations:

$$C_P = C_P' + 2[Cl_2Pd(P-PS)_2] + [Cl_2Pdpy(P-PS)] \quad (3)$$

$$C_{py} = [Cl_2Pdpy(P-PS)] \quad (4)$$

$$C_{Pd} = [Cl_2Pd(P-PS)_2] + [Cl_2Pdpy(P-PS)] \quad (5)$$

Eliminating the two unknown quantities we obtain the relation

$$C_{Pd} = \frac{1}{2}(C_P + C_{py} - C_P') \quad (6)$$

It is now pleasing to note that when plotting  $C_{Pd}$  against  $C_P + C_{py}$  for the resins PI and PIII treated with  $Cl_2Pd(pyridine)_2$ , two straight lines result (Fig. 6). The slope of these

lines are 0.5 as in formula (6) and the intercept with the abscissa axis give a value for  $C_P'$ .

One of the points for the resin PI falls beside the line. This point corresponds to the lowest metal loading and one can rather safely assume there is unused ('free') phosphine groups present besides the  $Cl_2Pd(P-PS)_2$  complexes. Hence eq. 3 is not satisfied.

It is easily realized that the requirement for neglecting the 'free' phosphine concentration is that  $C_{Pd}^O \geq (C_P^O - C_P') \frac{1}{2}$  where  $C_{Pd}^O$  and  $C_P^O$  are the starting values of the two concentrations.

Two interesting observations may now be made: The first one concerns the value of  $C_P'$ , the inaccessible phosphine concentration. Although we have only two points (or rather one, considering the final situation) for the polymer PII it is possible to calculate  $C_P'$  for this resin supposing that the relations of equations (3)-(5) holds. Such an assumption can be made rather safely as pyridine is detected to an appreciable extent. Thus introducing the analytical results into eqs. (3)-(5) one obtain  $C_P' = 0.46$  mmole/g.

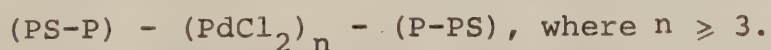
How does then the determined  $C_P'$  values correlate with the polymer structure? The determined BET surface area (Table 1) reflects the porosity of the polymer in dry state. That is, the higher the BET area the greater is the porosity. It is now pleasant to note that the smaller the surface area (the lower the porosity) the larger is the relative concentration of shielded phosphine groups, inaccessible for coordination (Table 1). This holds for polymers PI and PII, both of which are prepared by phosphination of a preformed polymer. Polymer PIII which is prepared by co-polymerisation of the monomers,



styrene, divinylbenzene and p-styrenediphenylphosphine does not, however, follow this pattern. Although this polymer has the lowest BET area the relative concentration of inaccessible phosphine groups is rather low. The reason for this might be the synthetic procedure. It is quite possible that the mode of preparation has created a polymer more prone to swell in the organic solvent used in the metal fixation. Hence the low porosity as reflected by the BET area in dry state might be drastically changed by the action of the solvent.

The second observation one might make concerns the PI resins treated with the benzonitrile complex. We assume that the value of  $C_p'$  is the same for the benzonitrile series as for the pyridine one. This can be rather safely done as the metal loading is about the same in the two cases. It is now possible to calculate the formal stoichiometric ratio Pd/P in the three experiments. In Table 3 this is done and one notes that in all cases but the one with the lowest metal content one gets more than one Pd for two P. Indeed the highest palladium content give Pd:P = 2.8:2.

From these observations one can deduce that there exists one or more species in the resin with the general formulation



The exact value of n cannot be determined without extra assumptions. Indeed, there might very well exist a series of complexes with  $n = 3, 4, 5$  and so on. What is important to point out here, however, is that this analysis of the total composition of the resins leads us to the same result as did the IR investigations on 4-cyanopyridine treated resins as well as the IR investigations on the Pd-Cl vibration modes.

## CONCLUSIONS

We can now summarize our results of this investigation. It is evident that the properties of the resin such as phosphine concentration and surface area are important for the nature of the complexes that may be formed on treating the polymer with metal salts or complexes. The nature of these resincomplexes will in its turn determine the catalytic properties of the resins. It is therefore of great importance to investigate the structure and metal ligand interactions in these complexes to be able to understand the detailed catalytic processes. In our work we have used the concept of 'inaccessible phosphine concentration'. It may be an object for further work to investigate synthetic routes by which unutilized phosphines are minimized. Another question relating to this effect is whether the 'inaccessible phosphine concentration' is constant or varies with the metal load or not.

Another very important discovery is that the resin can act as a host for  $(\text{PdCl}_2)_n$  chains linked to phosphine groups. Such chains may have properties similar to crystallites of  $\text{PdCl}_2$  rather than to bisphosphine complexes and therefore it will be important in further work to investigate if such chains are formed for high metal loading also from other complexes than  $\text{Cl}_2\text{Pd}(\text{benzonitrile})_2$ . E.g. the existence of these chains can be the reason for the easy reducibility of a part of Pd atoms in the resin.

The task for the catalyst designer is to combine the effects of crosslinking on diffusion of reactants and products with that on properties of the catalytically active metal complex.

## ACKNOWLEDGEMENT

This work was supported by grants from Styrelsen för Teknisk Utveckling (the Swedish Board for Technical Development). We also thank AB Karlshamns Oljefabriker for financial and technical support and Dr Bernd Rebenstorf, Chemical Center, LUND, for valuable discussions.



Table 1.

Phosphorus content and BET surface area for the polymers.

| Polymer                                                       | Denoted | %P  | $C_p$<br>(mmol/gram) | BET area<br>(m <sup>2</sup> /g)    | Cross-linking<br>(%) | $C_p'$<br>(mmol/gram) | $\frac{C_{p.100}}{C_p}$ |
|---------------------------------------------------------------|---------|-----|----------------------|------------------------------------|----------------------|-----------------------|-------------------------|
| Merck                                                         | PI      | 2.5 | 0.81                 | 53.5                               | 2                    | 0.28                  | 34                      |
| Pierce                                                        | PII     | 1.9 | 0.62                 | 1.5                                | 2                    | 0.46                  | 74                      |
| Styrene-<br>p-styrene<br>diphenyl-<br>phosphine<br>co-polymer | PIII    | 5.0 | 1.61                 | too small<br>to be de-<br>termined | 2                    | 0.50                  | 31                      |

Table 2.

Analytical results for the prepared catalysts.

| Preparation no | Polymer | Pd complex used                       | P: Pd | %Pd  | Pd<br>mmol<br>gram | %N    | N<br>mmol<br>gram | *<br>%P-<br>corr | P<br>corr<br>mmol<br>gram | P/Pd | N/Pd |
|----------------|---------|---------------------------------------|-------|------|--------------------|-------|-------------------|------------------|---------------------------|------|------|
| 011            | PIII    | $\text{Cl}_2\text{Pd}_{\text{py}_2}$  | 2.5:1 | 5.74 | 0.54               | <0.1  | -                 | 4.5              | 1.46                      | 2.22 | -    |
| 012            | PIII    | $\text{Cl}_2\text{Pd}_{\text{py}_2}$  | 1.3:1 | 7.95 | 0.75               | 0.96  | 0.69              | 4.1              | 1.32                      | 1.76 | 0.92 |
| 019            | PIII    | $\text{Cl}_2\text{Pd}_{\text{py}_2}$  | 0.6:1 | 8.56 | 0.80               | 1.11  | 0.79              | 4.0              | 1.29                      | 1.61 | 0.99 |
| 014            | PII     | $\text{Cl}_2\text{Pd}_{\text{py}_2}$  | 2.3:1 | 1.36 | 0.13               | 0.15  | 0.11              | 1.9              | 0.61                      | 4.7  | 0.85 |
| 015            | PII     | $\text{Cl}_2\text{Pd}_{\text{py}_2}$  | 1.1:1 | 1.37 | 0.13               | 0.16  | 0.11              | 1.9              | 0.61                      | 4.7  | 0.85 |
| 037            | PI      | $\text{Cl}_2\text{Pd}_{\text{py}_2}$  | 6:1   | 1.23 | 0.12               | <0.07 | -                 | 2.44             | 0.79                      | 6.5  | -    |
| 038            | PI      | $\text{Cl}_2\text{Pd}_{\text{py}_2}$  | 3:1   | 2.91 | 0.27               | <0.08 | -                 | 2.38             | 0.77                      | 2.8  | -    |
| 039            | PI      | $\text{Cl}_2\text{Pd}_{\text{py}_2}$  | 2:1   | 3.49 | 0.33               | 0.22  | 0.16              | 2.31             | 0.75                      | 2.3  | 0.49 |
| 040            | PI      | $\text{Cl}_2\text{Pd}_{\text{py}_2}$  | 1:1   | 4.19 | 0.39               | 0.50  | 0.36              | 2.23             | 0.72                      | 1.8  | 0.91 |
| 034            | PI      | $\text{Cl}_2\text{Pd}(\text{PhCN})_2$ | 3:1   | 2.58 | 0.24               | -     | -                 | 2.41             | 0.78                      | 3.2  | -    |
| 035            | PI      | $\text{Cl}_2\text{Pd}(\text{PhCN})_2$ | 2:1   | 3.64 | 0.34               | -     | -                 | 2.35             | 0.76                      | 2.2  | -    |
| 036            | PI      | $\text{Cl}_2\text{Pd}(\text{PhCN})_2$ | 1:1   | 6.64 | 0.62               | -     | -                 | 2.22             | 0.72                      | 1.2  | -    |

Table 3.

| Preparation | C <sub>Pd</sub><br>(mmol<br>gram) | C <sub>P<sub>tot</sub></sub><br>(mmol<br>gram) | C <sub>P<sub>inacc.</sub></sub><br>(mmol<br>gram) | Coordinated P<br>(mmol<br>gram) | Coordinated N<br>(mmol<br>gram) | ΣN+P<br>(mmol<br>gram) | Stoichiometry<br>Pd:ΣN+P |
|-------------|-----------------------------------|------------------------------------------------|---------------------------------------------------|---------------------------------|---------------------------------|------------------------|--------------------------|
| 011         | 0.54                              | 1.46                                           | 0.50                                              | 0.96                            | -                               | 0.96                   | 1:2                      |
| 012         | 0.75                              | 1.32                                           | 0.50                                              | 0.82                            | 0.69                            | 1.51                   | 1:2                      |
| 019         | 0.80                              | 1.29                                           | 0.50                                              | 0.79                            | 0.79                            | 1.58                   | 1:2                      |
| 037         | 0.12                              | 0.79                                           | 0.28                                              | -                               | -                               | 0.51                   | -                        |
| 038         | 0.27                              | 0.77                                           | 0.28                                              | 0.49                            | -                               | 0.49                   | 1:2                      |
| 039         | 0.33                              | 0.75                                           | 0.28                                              | 0.47                            | 0.16                            | 0.63                   | 1:2                      |
| 040         | 0.39                              | 0.72                                           | 0.28                                              | 0.44                            | 0.36                            | 0.80                   | 1:2                      |
| 034         | 0.24                              | 0.78                                           | 0.28                                              | 0.50                            | -                               | 0.50                   | 1:2                      |
| 035         | 0.34                              | 0.76                                           | 0.28                                              | 0.48                            | -                               | 0.48                   | 1.4:2                    |
| 036         | 0.62                              | 0.72                                           | 0.28                                              | 0.44                            | -                               | 0.44                   | 2.8:2                    |

## References

1. Grubbs, R.H. and Sweet, E.M, Macro mol. 8, 241, (1975).
2. Grubbs, R.H. and Su, S.H., in "Organomet. Polymers" (Carraher, C.E. Jr., Sheats, I.E. and Pittman, C. U., Jr., Eds.) Academic Press, New York, 1978.
3. Somoano, R.B., Gupta, A., Volksen, W., Rembaum, A. and Williams, R. Ibid.
4. Kuznetsov, B.N. in "Relations entre catalyse homogène et catalyse hétérogène" (CNRS Ed.) CNRS, Paris, 1978.
5. Purcell, K.F. and Kotz, I.C., "Inorganic Chemistry" p. 899 W.B. Saunders Company, 1977.
6. Rebenstorf, B. and Larsson, R, Z. Anorg. Allg. Chemie. 453, 127, (1979).
7. Rebenstorf, B. and Larsson, R., Ibid. 453, 139, (1979).
8. Andersson, C. and Larsson, R., Submitted to J. Am. Oil. Chem. Soc.
9. Bruner, H. and Bailar, J.C., Jr., J. Am. Oil. Chem. Soc. 49, 533, (1972).
10. Bruner, H. and Bailar, J.C., Jr., Inorg. Chem. 12, 1465, (1973).
11. Andersson, C. and Larsson, R., Chemica Scripta 15, 45 (1980).
12. Terasawa, M., Kaneda, K., Imanaka, T. and Teranishi, S., J. Catalysis 51, 406, (1978)



13. Kharasch, M.S., Seyler, R.C., and Mayo, F.R., J. Am. Chem. Soc. 60, 882, (1938).
14. Rabinowitz, R. and Marcus, R., J. Org. Chem. 26, 4157, (1961).
15. "Organic Phosphorus Compounds" (Kosolapoff, G.M. and Maier, L. Eds.) Vol 1, p. 298.
16. Pittman, C.U., Jr., Hirao, Quock Ng. Akira, Hannick, W. and Hanes, R. in "Relations entre catalyse homogène et catalyse hétérogène (CNRS Ed.) CNRS, Paris, 1978.
17. Pittman, C.U., Jr., Wu, S.K. and Jacobson, S.E., J. Catalysis 44, 87, (1976).
18. Fink, E., Compt. Rend. 126, 646, (1898).
19. Manchot, W., Ber. 58, 2518, (1925).
20. Irving, R.J. and Magnusson, E.A., J. Chem. Soc. 2283 (1958).
21. Fisher, E.O. and Vogler, A., J. Organomet. Chem. 3, 161, (1965).
22. Kushnikov, Yu. A., Beilina, A.Z. and Vozdrizhenskii, V.F., Russian J. of Inorg. Chem. 16, 218, (1971).
23. Colton, R., Farthing, R.H. and McCormick, M.J., Aust. J. Chem. 26, 2607, (1973).
24. Goggin, P.L. and Mink, I., I.C.S. Dalton Trans. 3, 534 (1974).
25. Hartley, F.R., "The Chemistry of Platinum and Palladium" p. 240 Applied Science Ltd, London, (1973).
26. Sanger, A.R., Schallig, L.R. and Gie Tan, K., Inorg. Chim. Acta 35, L 325, (1979).

27. Goodfellow, R.J., Goggin, P.L. and Venanzi, L.M. J. Chem. Soc. (A) 1897, (1967).
28. Adams, D.M., Goldstein, M. and Mooney, E.F., Trans. Faraday Soc. 59, 2228, (1963).
29. Wells, A.F., Z. Krist. 100, 189, (1938).

### Figure legends

Scheme 1: Possible reaction routes on treatment with a Lewis base L.

Scheme 2: Proposed reaction scheme for the preparation of polymer bound  $\text{Pd}^{2+}$ -complexes.

Fig. 1: IR-spectra of preparation 036 treated with CO

A direct after treatment

B after storage in air

C after treatment with moist solvent.

Fig. 2: Proposed reaction scheme for the CO-complexes formed in the resin.

Fig. 3: IR-spectrum of preparation 040 in the M-Cl region. (Wave numbers in  $\text{cm}^{-1}$ ).

Fig. 4: IR-spectra in the M-Cl region A: preparation 034, B: preparation 035, C: preparation 036, D: spectrum B with 5 times expanded abscissa scale, E: spectrum C with 5 times expanded abscissa scale. (Wave numbers in  $\text{cm}^{-1}$ ).

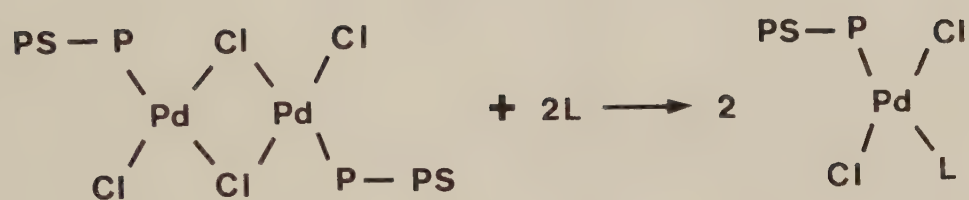
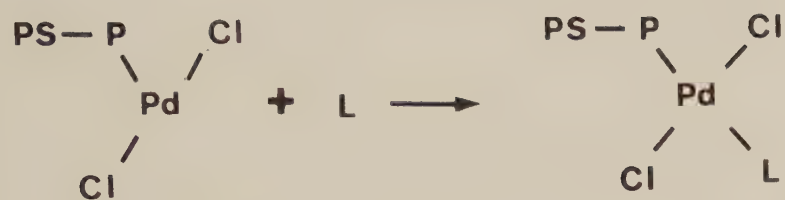
Fig. 5: Difference spectrum obtained on subtraction of the spectrum of preparation 039 from the spectrum of preparation 035. (Wave numbers in  $\text{cm}^{-1}$ ).

Fig. 6: Total palladium content plotted against the sum of total phosphine and pyridine content

polymer PI

polymer PIII

# Scheme 1





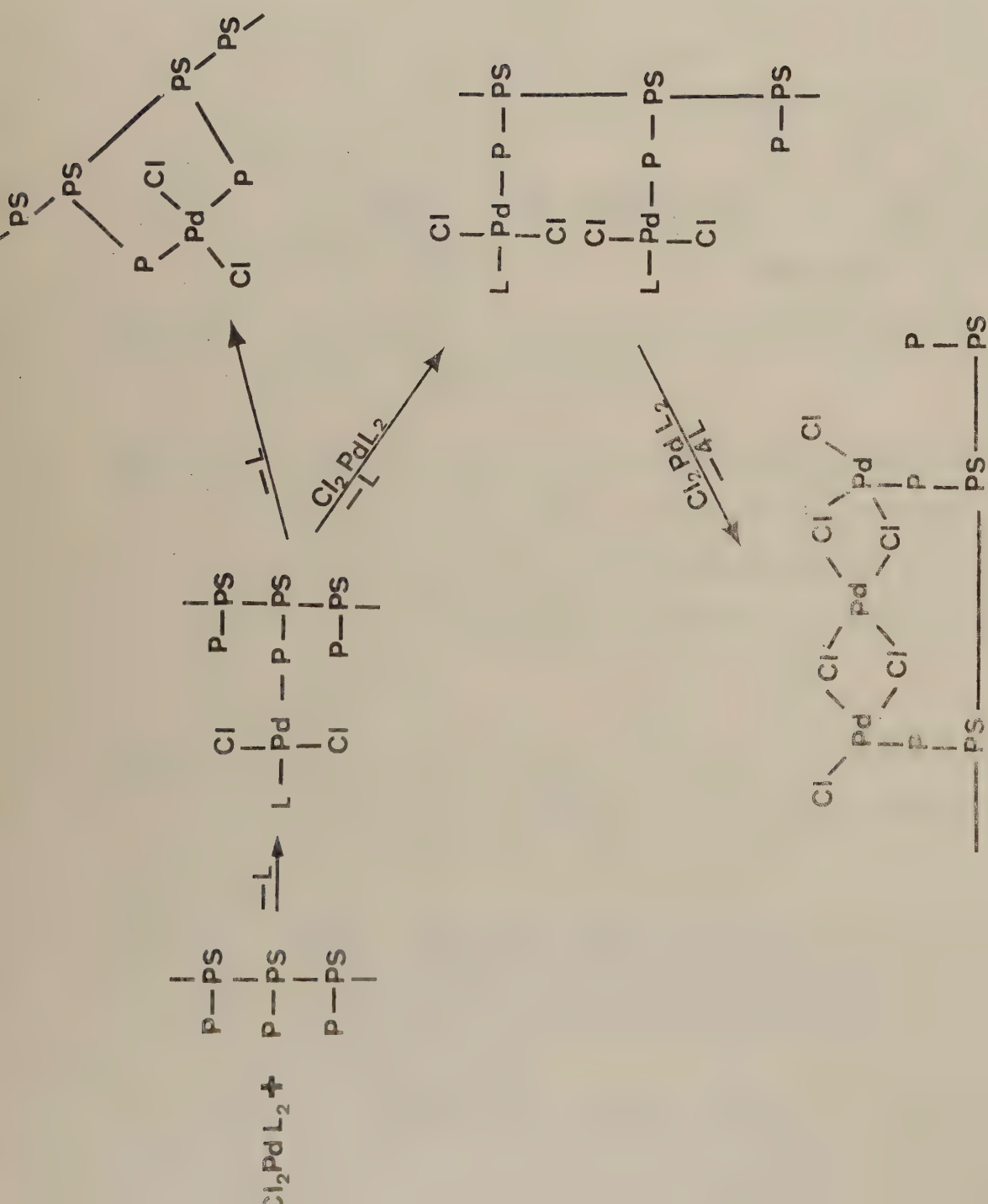


Fig 1



2200

2000

1800

Fig 2

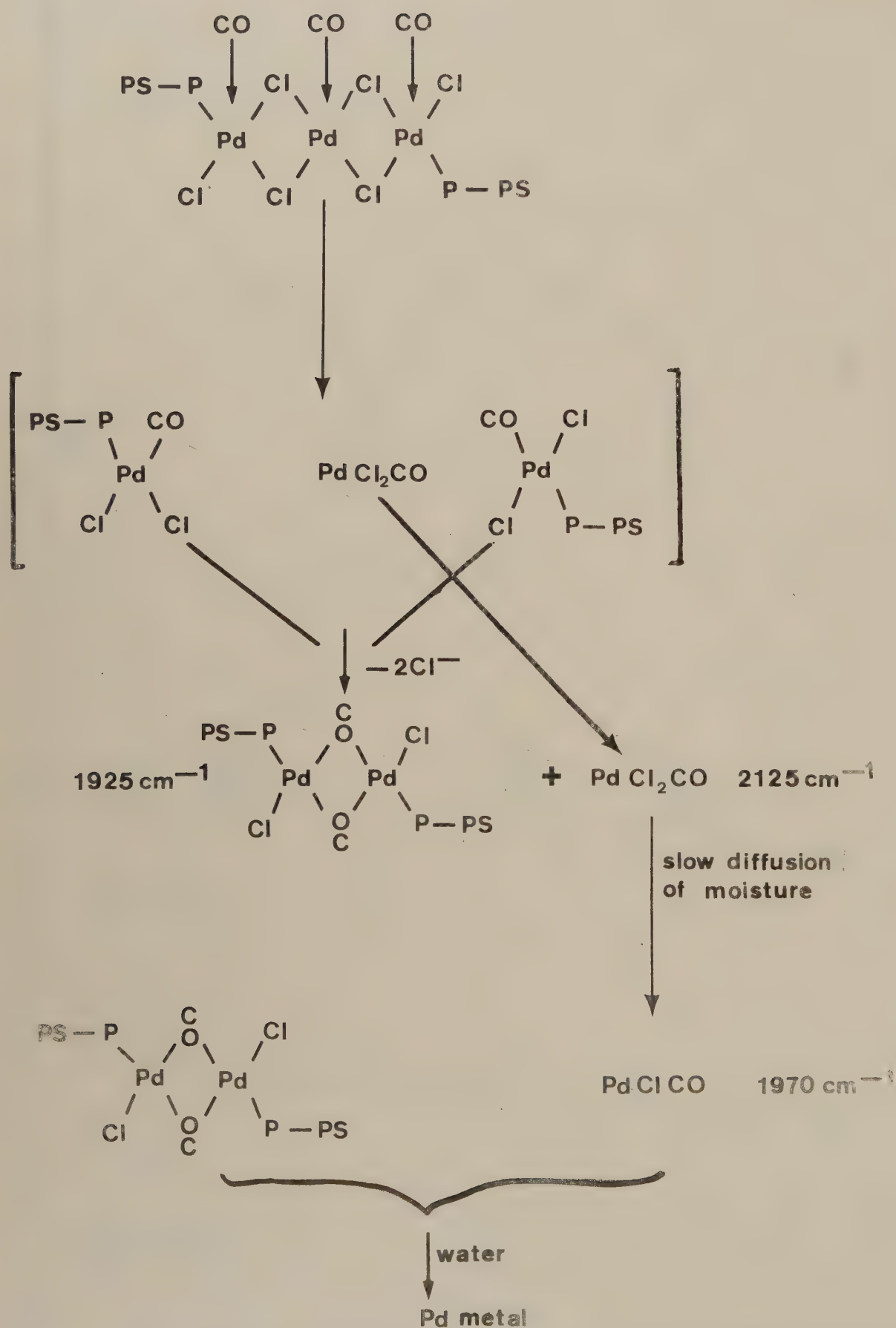


Fig 3

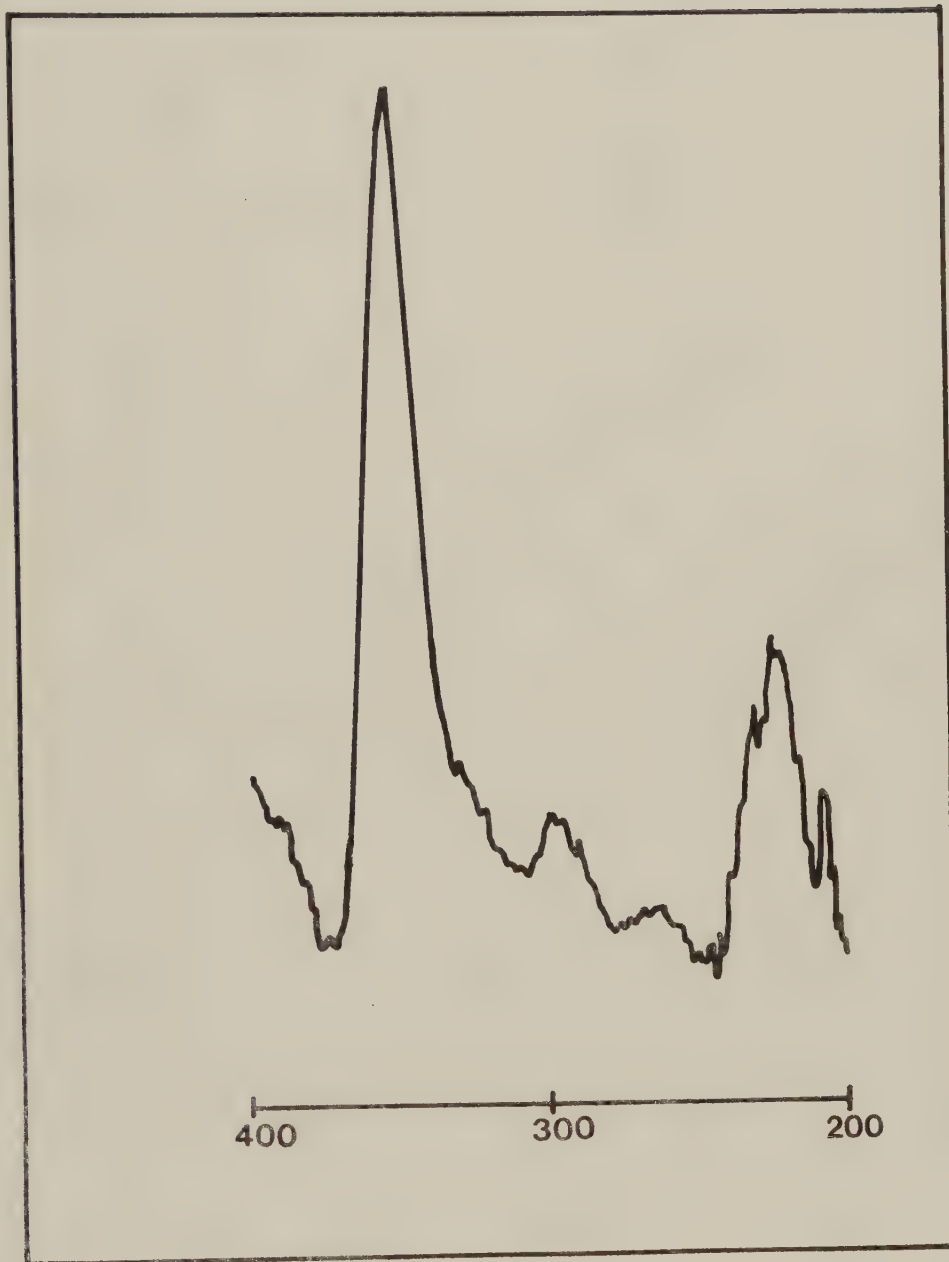




Fig 4

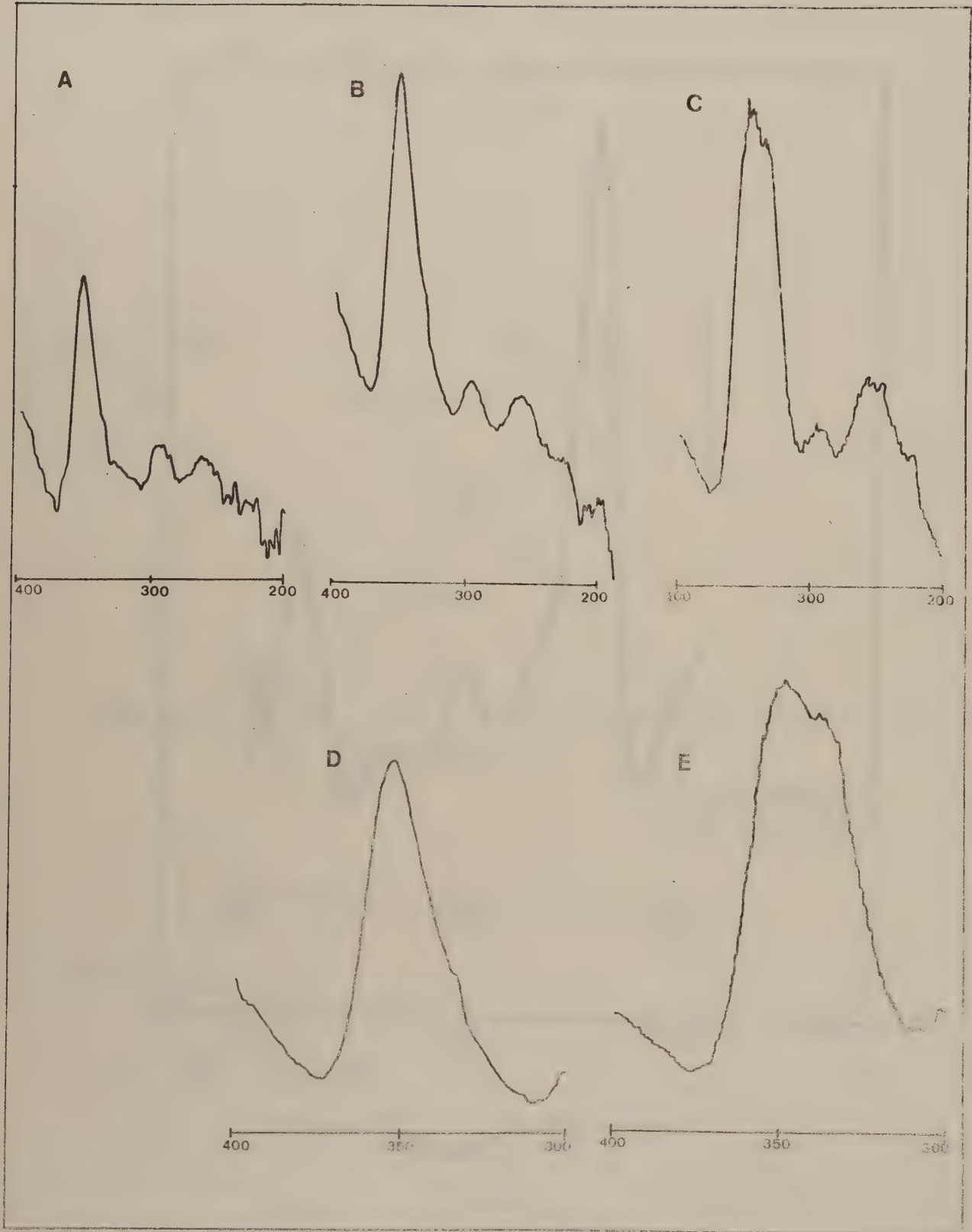


Fig 5

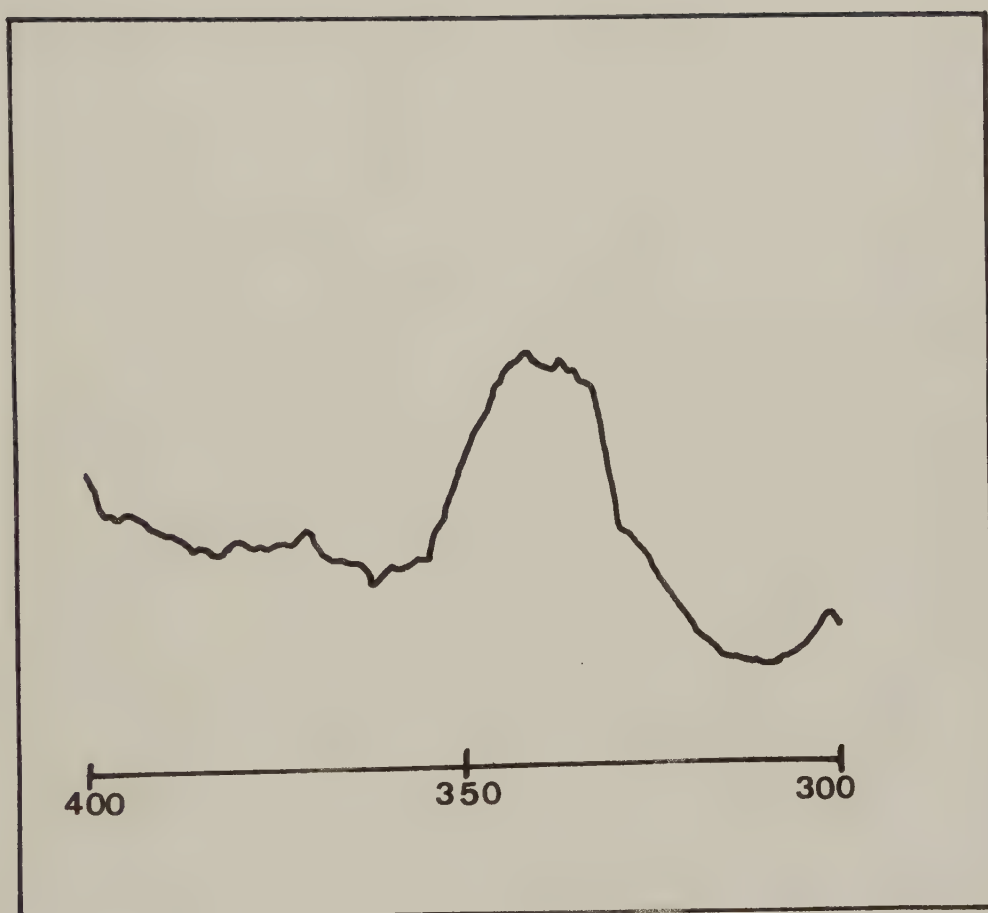
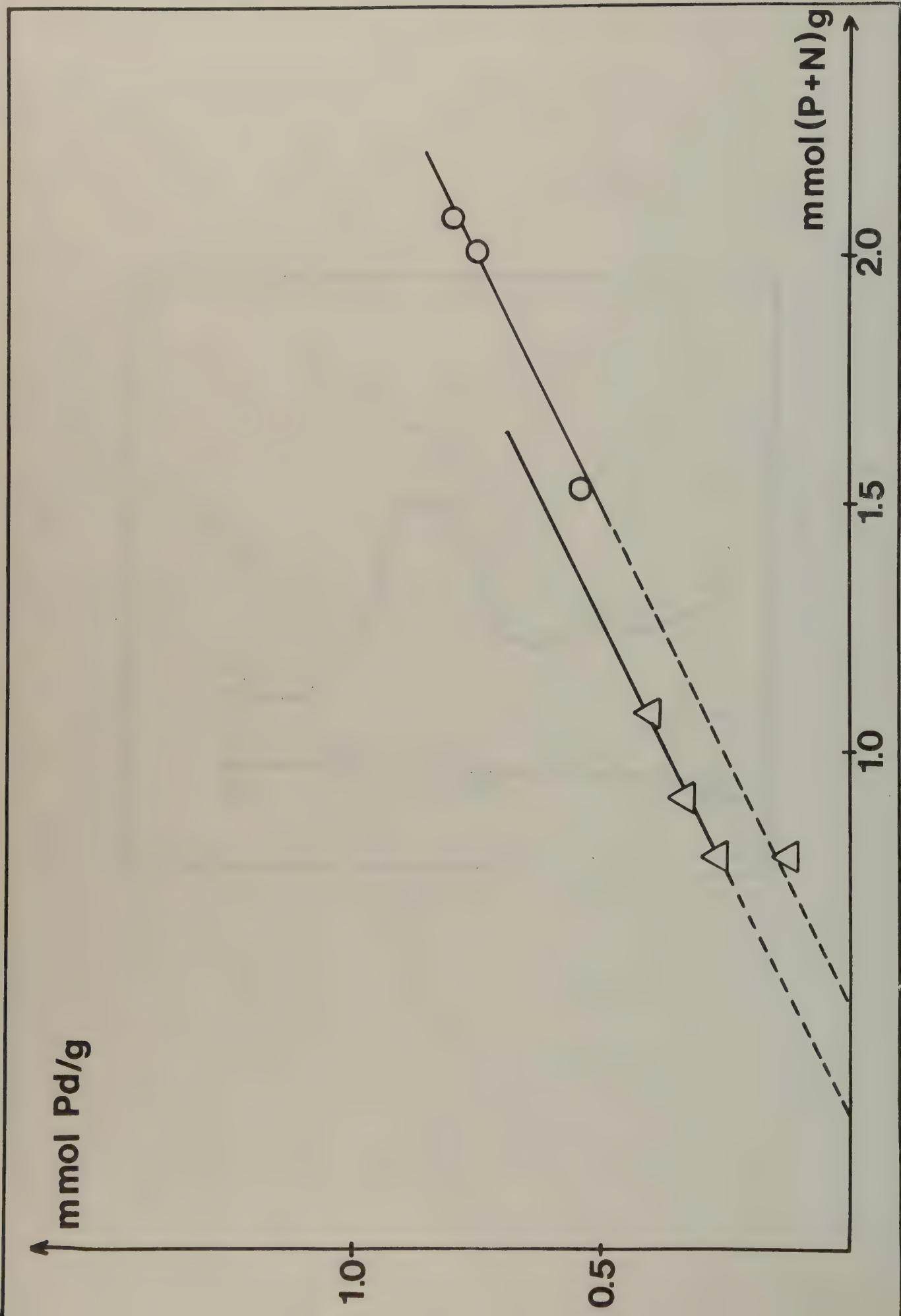


Fig 6



IV





Active sites in polymer-bound palladium -phosphine coordination catalysts. Chemical and XPS investigations.

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Running title: Active sites in polymer bound  
palladium catalysts.

# ABSTRACT

The nature of the activated state for polymerbound Pd catalysts have been studied. The investigation has been carried out using three different methods i.e. X-ray diffraction, XPS, and a chemical technique based on the redox couple benzoquinone/hydroquinone.

The chemical method shows that the activation is caused by a reduction of a part of the  $\text{Pd}^{2+}$  present in the resin. This method also gives a quantitative measure of the ratio  $\text{Pd}^{2+}/\text{Pd}^0$  in the activated catalyst.

Also the XPS investigation shows that the activation is due to a reduction of a part of the  $\text{Pd}^{2+}$  in the resin. This method is, however, not as sensitive and conclusive as the chemical one, due to formation of  $\text{PdO}_{\text{ads}}$  on the activated catalyst.

The X-ray diffraction study complements the other two methods in that it shows that the reduced Pd in the activated catalyst is Pd metal and not a low valent Pd complex.

How the formation of  $\text{PdO}_{\text{ads}}$  under the action of molecular oxygen is influencing the three methods used, is briefly discussed.

## INTRODUCTION

The attachment of coordination catalysts to porous polymers has attained increasing interest in recent years (1). This is motivated by the easier handling, i.e. catalyst separation and recovery, of the heterogenized system compared to the analogous system used in solution.

One of the first systems studied was  $\text{PdCl}_2$  bound to phosphinated polystyrene (2,3). This catalyst was used for the hydrogenation of methyl esters of fatty oils (2,3). The same system has also been used as catalyst in the oligomerization of butadiene (4) and for hydrogenation of olefins other than fatty oil methyl esters (5). We have also been studying this system and have found it to be a good catalyst for the hydrogenation of soybean oil (6). A common observation in all these studies is a change in colour - from yellow to green - of the catalyst after one or more catalytic runs. This colour change also appears after such treatments of the polymerbound catalyst, that makes it active under low pressure (1 atm). For the homogeneous counterpart no such activation can be achieved and it requires high pressures for operation. Different proposals as to the cause of this colour change of the catalyst have been made. Bruner (9) have suggested that the yellow to green change is caused by isomerisation reactions inside the polymer, resulting in bonding of the metal ion to non-adjacent phosphine groups. This in its turn is supposed to cause a weaker interaction between filled metal  $d_{z^2}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals with the electron rich benzene rings in the polymer. Terasawa et.al.(5) have discussed "the irreversible yellow to green colour change" in terms of solvent coordination. Oxygen containing solvents like dimethyl



formamide, ethanol, tetrahydrofuran and acetone gave the highest reaction rates in their study. Pittman et.al. (4) have claimed that it is the deposition of metallic Pd that is responsible for the colour change. We (6) have suggested that the activation is due to reduction of part of the  $\text{Pd}^{2+}$  ions in the resin. Since then we have continued our studies on this system in order to reach a better knowledge and understanding of the yellow to green change and the activation of the catalyst. In these studies we have been able to show (7,8) that the resin contains both the expected bisphosphine complex  $\text{Cl}_2\text{Pd}(\text{P-PS})_2$  as well as other species (P-PS = phosphinated styrene-divinylbenzene polymer). Depending on metal loading and synthetic route the relative proportions of these constituents vary. This situation is depicted in Fig. 1. The ratio X/Y is related to polymer properties such as surface area and phosphorus content and also to metal loading. Accepting the existence of these species in the resin, it is easy to understand that the heterogenized system behaves differently to the homogeneous system having  $\text{Cl}_2\text{Pd}(\text{PR}_3)_2$  as the sole component. However, from the catalytic point of view the important questions to rise are: How do these species behave under reaction conditions? Do they decompose or rearrange or stay intact? Do they influence the catalytic reaction at all? To answer these questions we have undertaken the study reported in this paper. We have limited our investigations to the catalysts prepared from  $\text{Cl}_2\text{Pd}(\text{benzonitrile})_2$ , with different metal loadings as these systems are more easily activated i.e. they demand a lower temperature for the activation compared to the complexes prepared from  $\text{Cl}_2\text{Pd}(\text{pyridine})_2$ . The "green activated catalysts" have been prepared by using different reducing agents such as  $\text{H}_2$ , CO. We have been especially interested to

determine whether "the activation" is due to reduction of  $\text{Pd}^{2+}$  or not. As X-ray photoelectron spectroscopy (XPS, ESCA) is a technique sensitive to changes in the chemical state of the atom concerned e.g. its oxidation state and mode of bonding it seemed to be the method of choice. XPS has been utilized before by other investigators to study polymer bound palladium-phosphine complexes (5,10). The difference in binding energy between used and fresh catalyst was found (5), however, to be very small, indicating only minor changes on activation. In addition to XPS studies we have therefore designed and applied another method, based on the redox couple quinone/hydroquinone, with the intention to check and perhaps extend the results obtained in the XPS investigations.

## EXPERIMENTAL

### Preparations.

The polymer bound palladium catalysts studied were prepared by ligand exchange (eq 2 fig. 1.). A detailed description of this procedure has been given elsewhere (8). The analytical data for the three preparations that have been investigated are given in Table 1.

### Activation.

To convert these catalysts to the "green" form they were treated with CO or  $\text{H}_2$  according to the following procedure: The catalyst samples (200 mg) were placed in a glass vessel. This was then evacuated to ca 1 torr and then filled with the appropriate gas to 750 torr. Acetone (10 ml) was then injected through a membrane. With  $\text{H}_2$  the catalyst samples changed colour within 5

minutes while CO required several hours to achieve the same colour change.

#### Reoxidation.

An acetone suspension of a weighed amount of the activated catalyst was treated with benzoquinone. The amount of benzoquinone added was equimolar to the total amount of Pd in the sample. This mixture was then stirred at room temperature until the catalyst had become yellow (ca 2 hours). The catalyst was separated and the solution analyzed for hydroquinone. To analyze the amount of hydroquinone formed on benzoquinone treatment the procedure of Joseph et.al. (12) was followed.

#### Instrumental.

XPS spectra were recorded with an AEI ES200 spectrometer using Al  $K_{\alpha}$  radiation. Various sampling techniques were examined. The best spectra were obtained with powdered samples pressed onto lead foils and this was used throughout this study.

The Cls peak mainly arising from the polymeric resin (phenyl and alkyl groups in the polymer) was used as an internal reference. To determine the binding energy of this reference the procedure of Larsson and Folkesson (11) i.e. infrared absorption intensity measurements of the C-H stretching vibration in the aromatic ring was used.

The type of resin we have used in this study (crosslinked polystyrene) can not be dissolved in any solvent. We have therefore used non-crosslinked polystyrene, which can be dissolved in e.g.  $CDCl_3$ , to determine the integrated absorption intensity. This intensity was found to be  $1880 \text{ M}^{-1} \text{ cm}^{-2}$ . Thus a value of 284.7 eV for the Cls binding energy can be calculated, using the



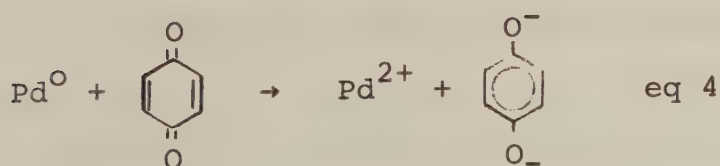
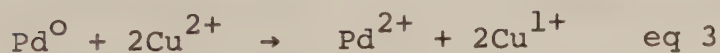
correlation graph of Folkesson and Larsson (11). Accordingly all binding energies reported in this study are corrected and referred to a Cls binding energy of 284.7 eV.

GLC analysis were done using a PE Fl7 gas chromatograph equipped with flame ionization detector.

Computer resolutions of the spectra were done with a Tektronix 4051 minicomputer. Programs were developed by Dr Roland Lykvist.

## RESULTS AND DISCUSSION

The various conditions described in literature ( $H_2$  or ethylen in methanol (9), butadien in THF (4),  $H_2$  in different solvents (5)) under which the yellow to green colour change and catalyst activation occur can all be described as reducing. The reduction of  $Pd^{2+}$  with  $H_2$ , e.g., is since long well known. Also alcohols like methanol and ethanol are known to reduce  $Pd^{2+}$  (13). Finally the reduction of  $Pd^{2+}$  under the action of ethylene and water in the Wacker process is well described. The most straightforward explanation of the catalyst activation is thus the appearance of a reduction of  $Pd^{2+}$  to  $Pd^0$ . From the Wacker chemistry it is however also known that the reduced Pd can easily be reoxidized with oxidating agents like  $CuCl_2$  or benzoquinone.



With this in mind we found it tempting to investigate if the



action of an oxidating agent on the green form of the catalyst would cause any change in colour. Indeed on reaction of the green  $H_2$  treated catalyst with  $CuCl_2$  in THF this substance reverted to the original yellow colour. The same thing also occurred when benzoquinone was used. This means that the activation of the catalyst is probably a reduction process and that the colour-change is not irreversible as has been claimed (9). The question then arises: Have previous investigators been mistaken? The XPS measurements of Terasawa et.al. (5) did not reveal any low valent Pd, neither did the  $CN^-$  test for  $Pd^0$  by Bruner (9) or our earlier investigation (6) give any evidence for Pd metal. If, however, only very limited amounts of  $Pd^0$  are formed on activation, the methods referred to would probably not reveal any  $Pd^0$ .

#### Chemical investigations.

However eq 4 states that the amount of hydroquinone formed equals the amount of  $Pd^0$  in the sample. Hence an analysis of the amount of hydroquinone formed after reaction of the activated catalyst with benzoquinone would give the amount of  $Pd^0$  originally present. We have accordingly treated our samples with benzoquinone in an acetone suspension and determined the amount of hydroquinone formed. The reason for choosing the couple benzoquinone/hydroquinone instead of  $Cu^{2+}/Cu^{1+}$  lies in the easier means by which hydroquinone can be determined. The results of this investigation are given in Table 2. From these data one can emphasize the following:

- 1) At the lowest metal loading the ratio  $Pd^0/Pd_{tot}$  is indeed very low (0.06). This is also reflected in the colour change of this catalyst. This had only a shade of green, while the

other two preparations changed colour completely.

- 2) Not only does the absolute amount of  $\text{Pd}^0$  increase on increased metal loading. So does also the ratio  $\text{Pd}^0/\text{Pd}_{\text{tot}}$ . This fact indicates that the metal content is influencing the reducability.
- 3) The increase in the ratio  $\text{Pd}^0/\text{Pd}_{\text{tot}}$  parallels the increase in the ratio  $Y/X$  (eq 2). Hence one can suggest that the reduction of  $\text{Pd}^{2+}$  is not a reduction of the palladium in the bisphosphine complex  $\text{Cl}_2\text{Pd}(\text{P-PS})_2$  but that it is the bridged specimen that is reacting. This is not surprising since palladium coordinated to two phosphine groups in complexes like e.g.  $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$  are known to withstand reducing conditions. The bridged complex on the other hand is very similar to solid  $\text{PdCl}_2$ , which is built up by chloride bridged  $\text{PdCl}_2$  units (13) and solid  $\text{PdCl}_2$  is easily reduced by  $\text{H}_2$ .
- 4) For preparation 034 the existence of the species  $\text{PS-P}-(\text{PdCl}_2)_n\text{-P-PS}$  in the resin could not be proved in our earlier investigation of this system (8). Neither from analytical data nor from spectroscopic studies, e.g., IR studies in the metal-chlorine stretching region. However the fact that even for this preparation, with a low metal content, some  $\text{Pd}^0$  is formed on treatment with reducing agents indicates that it probably also contains the bridged complex.
- 5) In the discussion above the reduced Pd has been termed  $\text{Pd}^0$ . This does not however have to stand for palladium metal. The reoxidizing procedure described does not tell if it is Pd-metal or  $\text{Pd}^0$  complexes that act as the electron donor towards benzoquinone. All we can say is that a redox process has taken place. This then makes it necessary to use other methods to elucidate the system further.

Since much of the research work that is done at our laboratory is directed towards applications of XPS on catalyst problems we have used this method for further studies.

#### XPS-studies.

The procedure outlined in the proceeding section i.e. treatment of the samples with a reducing agent and reoxidizing with benzoquinone ought, at least in theory, be easily followed by XPS measurements. This statement is based upon the energy difference between the Pd 3d bands in  $\text{Pd}^{2+}$  phosphine complexes (e.g.  $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$   $E_{\text{b}}3\text{d}_{5/2} = 337.9$  eV (14)) and Pd metal ( $E_{\text{b}}3\text{d}_{5/2} = 335.2$  (15)). This energy difference is relatively large (2.7 eV) and in fact so large that with normal FWHM of around 2 eV these bands should be well separated (16).

For our three samples (034, 035, 036) differentiating in metal content we have examined first the untreated ones (A), then the same samples treated with reducing agent (B) and finally the latter ones treated with benzoquinone (C). For the sake of clarity we will discuss the XPS measurements under the categories A, B, and C.

#### A. Untreated samples.

These were the first samples examined. They all gave the same band shape and Pd 3d binding energy independent of metal content ( $337.9 \pm 0.2$  eV). A typical spectrum is shown in Figure 2a. The measured Pd binding energy corresponds to what is normally found for  $\text{Pd}^{2+}$  complexes with monomeric phosphine ligands (14). The difference in composition (different Y/X ratios eq 2) is not reflected in our measured binding energies. This indicates that the difference in Pd 3d binding energy for  $\text{Cl}_2\text{Pd}(\text{P-PS})_2$  and



PS-P-(PdCl<sub>2</sub>)<sub>n</sub>-P-PS is small, (within experimental errors) and hence that XPS can not be used to determine the Y/X ratio.

Terasawa et.al. have also observed (10) that the Pd 3d energy binding for polymerbound complexes is relatively insensitive to the type of species in the resin.

#### B. Samples treated with reducing agents.

The spectra obtained with our three different samples after reducing treatment were broad and with no direct sign of any shoulders (Fig. 2b). This is the same general pattern as that found earlier (5) for polymerbound palladium catalysts after they had been used in hydrogenation experiments. For the sample (034) with the lowest metal content no shift in binding energy relative to the binding energy of the same untreated sample could be observed. Nor was the line broadening significant. Hence the very small part of low valent Pd, that the chemical investigation had shown, was not revealed in the spectrum of this catalyst.

Even for the catalyst with the intermediate metal content the conditions were the same, i.e. no significant binding energy shift or band broadening after treatment with a reducing agent could be observed. One thing that should be noted in this connection is that the two samples related, due to low metal content give spectra of a quality not suited for a detailed analysis. It is therefore quite possible that with a better signal to noise ratio more information could have been gained. However, for the sample with the highest metal content (036) better spectra were obtained and in these spectra the position of the Pd 3d<sub>3/2</sub> and 3d<sub>5/2</sub> bands was shifted 0.5 eV towards lower binding energy relative the same untreated sample (Fig. 2c). These



bands were also 0.3 eV broader than the bands obtained with the untreated sample. Two things can be stated from this observation. Firstly, also XPS indicates that the activation is caused by a reduction of  $\text{Pd}^{2+}$  since lowered binding energy means lowered oxidation state. Secondly as no shoulder, only broadening of the band was observed, these bands do not fit to a mixture of  $\text{Pd}^{2+}$  and Pd metal (14). Neither do they appear at the binding energy corresponding to pure Pd metal. When computerized spectrum resolution procedures were applied to this spectrum the best fit was obtained with one band at  $E_b = 338.0$  and another at 336.7 eV. This resolution is shown in Figure 3a. The band at the highest energy (338.0 eV) falls at the position for normal  $\text{Pd}^{2+}$  while the band at 336.7 is about 1.5 eV higher than expected for Pd metal. This result then contradicts the interpretation made for the result of the chemical investigation, namely that Pd metal is the product formed on activation. This discrepancy motivated a renewed investigation and since the sample with the highest metal content was the one best suited for XPS-studies we concentrated on this. Consequently, a new sample was treated with CO as done before, but this time the XPS investigation was done before the chemical investigation. The spectrum (Fig. 2d) obtained this time showed interesting changes compared to that obtained earlier. As can be seen from a comparison of figures 2c and 2d the band maxima has moved 0.6 eV towards lower binding energy and in addition the 3d<sub>5/2</sub> band in figure 2d now shows a skewness indicating a peak at around 337.7 eV. The same spectrum resolution procedure was also applied to this new spectrum. The result of this is shown in Figure 3b. Also in this case two bands gives the best fit.

One at the same position as earlier 337.9 eV, but the low energy band now appears at 336.1 eV instead of 336.7 as was the case in the first spectrum (3a). The only experimental condition that was changed between the two spectra obtained was the time elapsed between the registration of the spectrum and the treatment with CO. In the first-mentioned experiment, the spectrum was recorded 2 days after the CO-treatment while in the second experiment the spectrum was recorded only a few hours after the CO-treatment. Therefore we recorded the spectrum of the second sample with different time intervals. Between the recordings the sample was kept outside the spectrometer in the open air. The result of this was really that changes in the registered spectrum took place and that a state of equilibrium was reached after 1 day. This "equilibrium spectrum" was identical to that obtained in the first investigation of sample 036. From these observations one can conclude that the changes taking place when the reduced samples is kept in air is most likely an oxidation of Pd by molecular oxygen. Hence what we observe in the "equilibrium spectrum" is in fact a mixture of  $\text{Pd}^{2+}$  bound to phosphine groups in the resin and Pd oxide of some form. If we now return to our resolved spectra in figures 3a and 3b the binding energy of the band at 336.7 eV (fig. 3a) corresponds to what has been found for  $\text{PdO}$  (17). At the same time one notices that the difference in binding energy between the low energy band in fig. 3a (336.7 eV) and the low energy band in fig. 3b (336.1 eV) is 0.6 eV. This is the same energy difference as that found for Pd metal and  $\text{PdO}_{\text{ads}}$  (17), although at slightly different position on the energy scale. Hence from these observations it can not be safely stated if

it is the bulk oxide or the surface oxide that is formed. This problem will however be discussed on page 16. The whole experimental sequence described above illustrates rather nicely one problem often met in catalytic studies: How to recover and transfer the catalyst from its working conditions to the conditions necessary for instrumental analysis without disturbing or changing the catalyst. In our case the catalyst was not protected from such changes and consequently what we first studied was not the actual catalyst but a chemically different one. However, our XPS instrument is equipped with a sample preparation chamber which makes it possible to perform the gas-treatment ( $\text{CO}$  or  $\text{H}_2$ ) and spectrum recording without having to expose the sample to air. However, when performing such an experiment no colour change was found and the spectrum registered after treatment with  $\text{H}_2$  at 1 atm for 24 hours was unchanged relative to that of an untreated sample. Hence no reaction had taken place, and the reason for this is unknown. It might well be so that solvent assistance is necessary in the reduction, since solvent effects on the catalytic activity have been noted (5). An alternative explanation is that gas diffusion into the sample is limited due to the compact structure of the sample pressed onto the lead foil.

#### C. Sample treated with benzoquinone.

When our three different samples after reduction was subjected to the benzoquinone treatment they all reversed to their yellow colour. For the sample with the highest metal content this reaction was also reflected in the XPS spectrum. In the spectrum obtained for this sample the  $\text{Pd } 3d_{3/2}$  and  $3d_{5/2}$  binding energies are the same as those measured for the



same untreated sample. Hence the benzoquinone treatment does oxidize the sampel back to the original oxidation state. This does not implicate, however, that the original structure is restored. On the contrary it is most likely that this is not the case. As we have used the benzoquinone treatment only as an aid to determine the amount of  $\text{Pd}^0$  in the resin the structure is unimportant, however.

As no change in binding energy was noted, after the reductive treatment of the other two samples, no change in binding energy was expected after the reoxidation. This was also the case.

In Figure 4 we have collected our measured binding energies for all our samples exposed to the different treatments related above. For the sample with the highest metal content this gives a rather clear-cut illustration of the redox process, both the intended one, with catalyst activation and reoxidation, and the unintended air oxidation. It also illustrates the limits of the XPS method, in this special case, since for the two other samples with low metal content no changes are observable. In this connection one other thing worth mentioning is the following: Since the XPS method and the chemical method both give the same qualitative result for the sample with the high metal content it can be concluded that the chemical method devised can be used to detect  $\text{Pd}^0$ . As to the quantitative results of the two methods used, these are not the same. (Compare band height 336.1 eV/337.8 eV with Table 2). This is understandable as XPS gives the surface composition but the chemical method gives bulk composition and these are probably not the same.



### The formation of Pd-oxide

In the preceding section it was suggested that the time dependent changes in the Pd  $3d_{3/2}$  and  $3d_{5/2}$  bands observed was caused by an oxidation of Pd metal to palladium oxide of some form. In the resolved spectra this showed up as a change in one of the components from 336.1 eV to 336.7 eV, while the other remained at its original position. The oxidation of metallic Pd, by molecular oxygen is however known to proceed first at higher temperatures. Lam and Boudart (18) observed an increased dioxygen uptake at 538 K in their study of small palladium particles. Paryjczak et. al. (19) observed three different temperature ranges for the reaction of dioxygen with Pd supported on alumina or silica. Range I (300-470 K) in which surface chemisorption occurs, range II (470-770 K) in which bulk metal oxidation occurs. As we have not used elevated temperatures, but kept our samples in air at room temperature only, it is likely that the band we observe at 336.7 eV can be assigned to  $\text{PdO}_{\text{ads}}$ .

We have, however, also used the X-ray powder method to study the sample (036 treated with CO) for which the change in the XPS spectrum was observed. In figure 5 the diffraction pattern of this preparation is given. This figure shows exclusively diffraction peaks of Pd metal. No trace of Pd oxide can be observed, although this sample had been kept in air several weeks. The fact that no oxide can be detected by X-ray diffraction studies supports the interpretation that it is the surface oxide that is formed. As X-ray diffraction is a bulk method giving information on the whole sample, the surface oxide is probably too small a part of the total Pd to be observed with

this method. XPS on the other hand is a surface method penetrating the sample to a depth of ca 20 Å (23), and will thus probably sense only the oxide. Consequently the results obtained by the two methods used, do not have to be the same.

In the X-ray diffraction study by Boudart (18) it was shown that palladium oxide can be easily reduced by reacting with dihydrogen at room temperature. This then gives another possibility to check if its palladium oxide we observe in our XPS investigation. By letting the same sample as that used in the X-ray diffraction experiment, react with dihydrogen (1 atm) in the ESCA sample preparation chamber we obtained a spectrum almost identical to that we obtained directly after the CO-treatment (fig. 2d). That the changes in XPS-spectra, that result from air exposure of the sample, can be reversed by treatment with dihydrogen shows that it is an oxide we are dealing with.

This oxidation of Pd metal by air does not only influence the XPS-investigations. It also interferes with the chemical method used in this study, since the amount of hydroquinone formed will not correspond to the amount of Pd metal originally present. The figures in Table 2 should therefore be interpreted with this in mind. However, the amount of Pd oxidized by air in our analysis is presumably very small since no oxide could be detected in the X-ray diffraction investigation. Also the  $\text{CN}^-$  treatment for the qualitative determination of Pd metal devised by Bruner (9) must be sensitive to air oxidation of Pd. The fact that no Pd metal was found in his work might be due to this phenomenon.

The position of the bands assigned to Pd(metal) and PdO<sub>ads</sub>

In our resolved spectra in figures 3a and 3b the bands at 336.7 (3a) and 336.1 (3b) was assigned to PdO<sub>ads</sub> and Pd metal respectively. These values are, however, about 1 eV higher than what is normally found for Pd 3d<sub>5/2</sub> (Pd metal  $E_b=335.2$  (15)  $E_b=335.0$  (17), PdO<sub>ads</sub>  $E_b=335.6$  (17)). Other investigators (14, 21) have, however, found values ( $E_b$  Pd 3d<sub>5/2</sub> for Pd metal= 335.8 eV) closer to that we found in figure 3b. We have recorded the spectrum for a Pd-foil and for a commercial Pd on carbon catalyst (Engelhardt's) and found binding energies for Pd 3d<sub>5/2</sub> of 335.2 eV and 335.8 eV, respectively. Several reasons for the rather high value we have found can be suggested. One obvious explanation concerns the problem of sample charging and the calibration method. For the Pd-foil which is a conductor no charging will interfere but for the Pd on carbon catalyst as well as with our Pd, bound to the polymer resin, sample charging might cause problems. The usual manner to compensate for sample charging is to refer measured binding energies to the binding energy of Cls in pumpoil deposits (285.0 eV). One then assumes that the charging of the pumpoil carbonaceous deposits and the sample is the same. In this study we have used a more elaborated method (11) to compensate for sample charging. This method uses an internal standard (the phenyl rings in the polymer) and the binding energy of this standard is indirectly determined by an infrared technique. This method has proved useful in several investigations (20) and for the Pd<sup>2+</sup> part in our samples it gives results in accordance to what is found for monomeric Pd<sup>2+</sup> phosphine complexes. The Pd<sup>2+</sup> part in our samples



are bound to the resin and is thus contained in the resin phase. Hence the potential sensed by the  $\text{Pd}^{2+}$  ion is most likely the same as that sensed by the phenyl groups of the resin. The small metallic particles in the resin on the other hand can be regarded as a separate phase, and thus their potential does not have to be the same as that of the resin. So the method of calibration might be the reason for the high value found for Pd metal and  $\text{PdO}_{\text{ads}}$ , the binding energies found for these two items being really ~1.0 eV lower than those recorded here.

#### CONCLUSION

Different methods have been used to elucidate the composition of the activated state for a palladium complex bound to phosphinated polystyrene resin. X-ray diffraction shows that metallic palladium is formed on activation of the catalyst. However, from both the chemical and the XPS investigation it can be concluded that the reduction to the metallic state involves only a part of the  $\text{Pd}^{2+}$  originally present in the resin. This holds for the catalyst with the highest metal loading. For the other two catalysts investigated, the concentration of the metallic phase is too low to be clearly shown by other methods than the chemical one. Since the chemical method doesn't tell what type of low-valent palladium that is formed, however, the three methods used complement each other.

One other thing that must be stressed in this connection is the disturbing action of molecular oxygen in oxidizing Pd to  $\text{PdO}_{\text{ads}}$ . This is perhaps most relevant in the XPS investigations, since XPS is the surface sensitive method, and consequently



the oxidation to  $\text{PdO}_{\text{ads}}$  will make an identification of Pd metal in the XPS spectrum more difficult or even impossible. This reaction with  $\text{O}_2$  is most likely one of the reasons for the somewhat limited results we have obtained by the XPS investigation. Even the chemical method is sensitive to oxidation by  $\text{O}_2$  in the air, but to a more limited extent. This is because this method gives bulk composition and Pd oxidation is probably important only at the catalyst surface.

With the catalyst composition derived at in this study the catalyst can be said to possess two different active sites in the same catalyst particle: Metallic Pd, which is known to activate molecular hydrogen easily and to function as a hydrogenation catalyst, and in addition also the hydrogenation catalyst  $\text{Cl}_2\text{Pd}(\text{P-PS})_2$ . A natural question to ask is then: How does this situation influence the catalytic activity and selectivity? To get activity and selectivity data one must perform detailed hydrogenation experiments. In order to discuss the results, however, a mapping of the components of the catalytic system as described in this investigation is needed. Referring to the present system, detailed knowledge of the variation of kinetic parameters with the ratio Pd metal/ $\text{Pd}^{2+}$  would be of great interest. It is, e.g. not very likely that  $\text{Cl}_2\text{Pd}(\text{P-PS})_2$  alone should be the active component under the mild conditions often used in connection with this catalyst. Its homogeneous counterpart needs high pressures to operate (22) and we have shown in an other study (7) that the polymer linked Pd catalyst with  $\text{Cl}_2\text{Pd}(\text{P-PS})_2$  as the sole component is inactive for the hydrogenation of soybean oil. Instead much of the information available at present indicates that it is the combination of the

two components that gives this catalyst its features. This question is, however, by no means settled, but opened for further investigations.

#### ACKNOWLEDGMENTS

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References:

1. Hartley, F.R. and Vezey, P.N., Adv. Organomet. Chem. 15, 189 (1977).
2. Bruner, H.S. and Bailar, J.C. Jr, J. Am. Oil Chem. Soc. 49, 533 (1972).
3. Bruner, H.S. and Bailar, J.C. Jr, Inorg. Chem. 12, 1465, (1973).
4. Pittman, C.U. Jr, Wu, S.K. and Jacobsen, E.S., J. Cat. 44, 87 (1976).
5. Terasawa, M. Kaneda, K., Imanaka, T. and Teranishi, S., J. Cat. 51, 406 (1978).
6. Andersson, C. and Larsson, R., Chemica Scripta 15, 45 (1980)
7. Andersson, C. and Larsson, R., Submitted to J. Am. Oil Chem. Soc.
8. Andersson, C. and Larsson, R., To be submitted to J. Cat.
9. Bruner, H., Thesis University of Illinois.
10. Terasawa, M., Sano, K., Kaneda, K., Imanaka, T. and Teranishi, S., J. Chem. Comm. 650 (1978).
11. Larsson, R. and Folkesson, B., Chemica Scripta 9, 148 (1976).
12. Joseph, H.M. and Andrzejczak, J., Isr. J. Chem. 11, 599 (1973).
13. Hartley, F.R., The Chemistry of Platinum and Palladium, p. 172, Applied Science, London, 1973
14. Kumar, G., Blackburn, J.R., Albridge, R.G., Moddeman, W.E. and Jones, M.M., Inorg. Chem. 11, 296 (1972).

- 15.a) Schön, G., J. Electron Spectroscopy 1 (1972-73).
- b) Fuggle, J.C. and Mårtensson, N., J. Electron Spectrosc. Relat. Phenom 21, 275 (1980).
16. ESCA applied to free molecules, Siegbahn, K., Nordling, C., Johansson, G., Hedman, J., Hedén, P.F., Hamrin, K., Gelius, U., Bergmark, T., Werme, L.O., Manne, R. and Baer, Y., p. 168, North-Holland, Amsterdam, 1971.
17. Kim, K.S., Grossman, A.F. and Winograd, N., Analytical Chemistry 46, 197 (1974).
18. Lam, Y.L. and Boudart, M., J. Cat. 47, 393 (1977).
19. Paryjczak, T., Jozwiak, W.K. and Goralski, J., Journal of Chromatography 155, 9 (1978).
20. Larsson, R., Folkesson, B. and Lykvist, R., Chemica Scripta 13, 178 (1978-79).
21. Nefedov, V.I., Salyn, YA. V., Moiseev, I.I., Sadovskii, A.P., Berenbljum, A.S., Knizhnik, A.G. and Mund, S.L., Inorg. Chim. Acta 35, L 343-344 (1979).
22. Itatani, H. and Beilar, J.C., J. Am. Oil Chem. Soc. 44, 147 (1967).
23. Watson, R.E. and Perlamn, M.L., "X-ray Photoelectron Spectroscopy Applications to Metals and Alloys", Structure and Bonding, Vo. 24, p. 83, Springer, Berlin, 1975.



Table 1

Analytical Data of the Catalyst samples studied.

| Preparation no | % Pd | <u>mmol Pd</u><br>gram catalyst | % P  | <u>mmol P</u><br>gram catalyst | ratio<br>P/Pd |
|----------------|------|---------------------------------|------|--------------------------------|---------------|
| 034            | 2.58 | 0.24                            | 2.41 | 0.78                           | 3.22          |
| 035            | 3.64 | 0.34                            | 2.35 | 0.76                           | 2.20          |
| 036            | 6.64 | 0.62                            | 2.22 | 0.72                           | 1.15          |

Table 2

Analyzed amount of Pd<sup>0</sup> in the activated catalysts.

| Sample | Activated<br>by | Pd <sup>0</sup> percent<br>of total Pd | mmol Pd <sup>0</sup> /gram catalyst |
|--------|-----------------|----------------------------------------|-------------------------------------|
| 034    | H <sub>2</sub>  | 6.0                                    | 0.014                               |
| 035    | H <sub>2</sub>  | 11.0                                   | 0.037                               |
|        | CO              | 6.5                                    | 0.022                               |
| 036    | H <sub>2</sub>  | 25.9                                   | 0.160                               |
|        | CO              | 26.7                                   | 0.165                               |

## Figure legends

Fig. 1. The complexes formed in the phosphinated polystyrene resin

- a) the pyridine complex as starting material
- b) the benzonitrile complex as starting material

Fig. 2. Pd 3d XPS spectra

a: Untreated sample 035, b: sample 035 treated with  $H_2$ , c: sample 036 treated with CO, stored in air, d: sample 036 treated with CO, direct after treatment.

Fig. 3. Resolved Pd 3d XPS spectra

a: resolution of the spectrum in fig. 2c,  
b: resolution of the spectrum in fig. 2d.

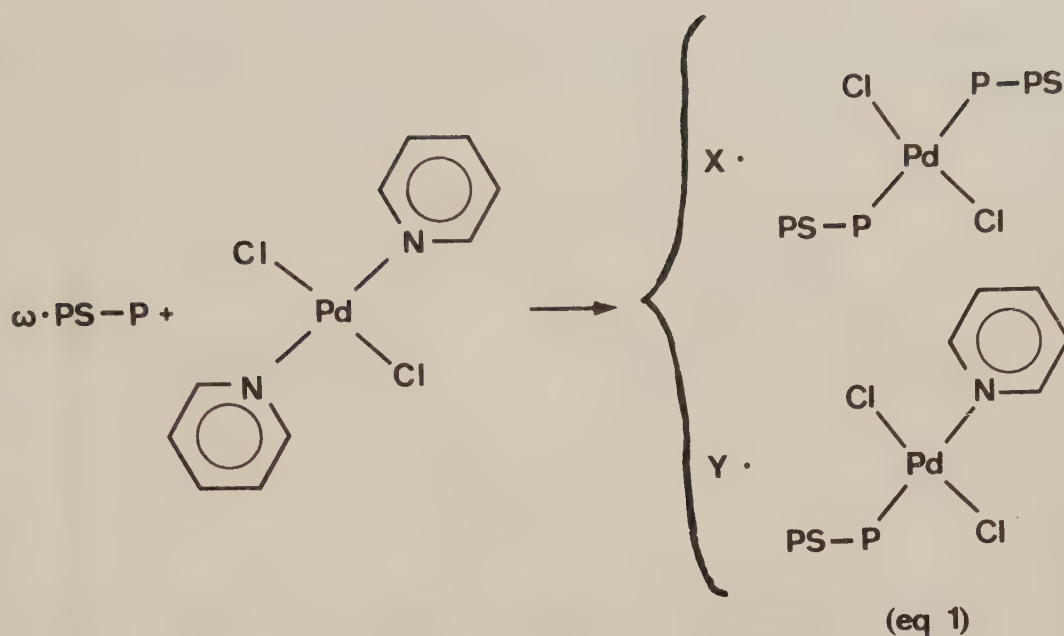
Fig. 4. Measured Pd 3d binding energies

(A) untreated 036. (B) 036 treated with CO, direct after treatment. (C) 036 treated with CO two hours after treatment. (D) 036 "equilibrium spectrum". (E) 036 treated with CO and reoxidized with benzoquinone. (F) untreated 035. (G) 035 treated with  $H_2$ . (H) 035 treated with CO reoxidized with benzoquinone. (I) 034 untreated.

Fig. 5. X-ray diffraction pattern of the sample 036 treated with CO and exposed to air.

Fig 1

A.



B.

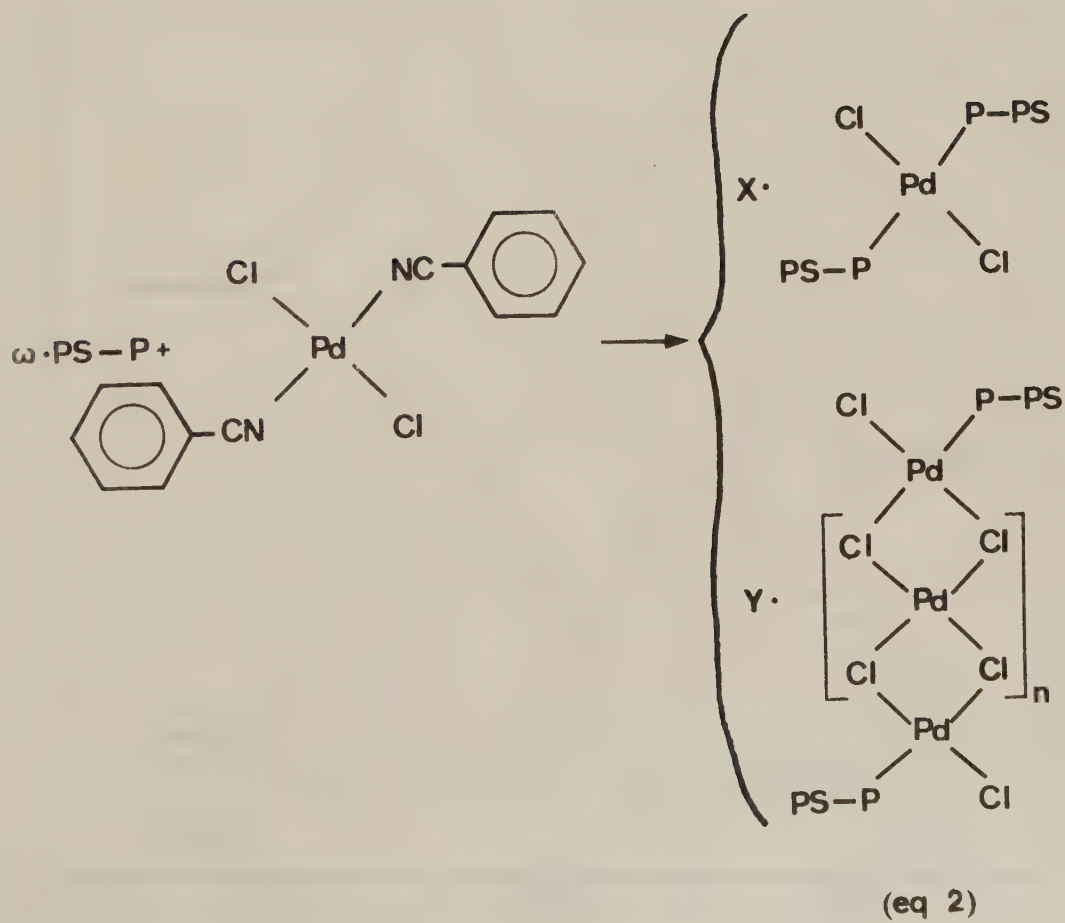




Fig 2

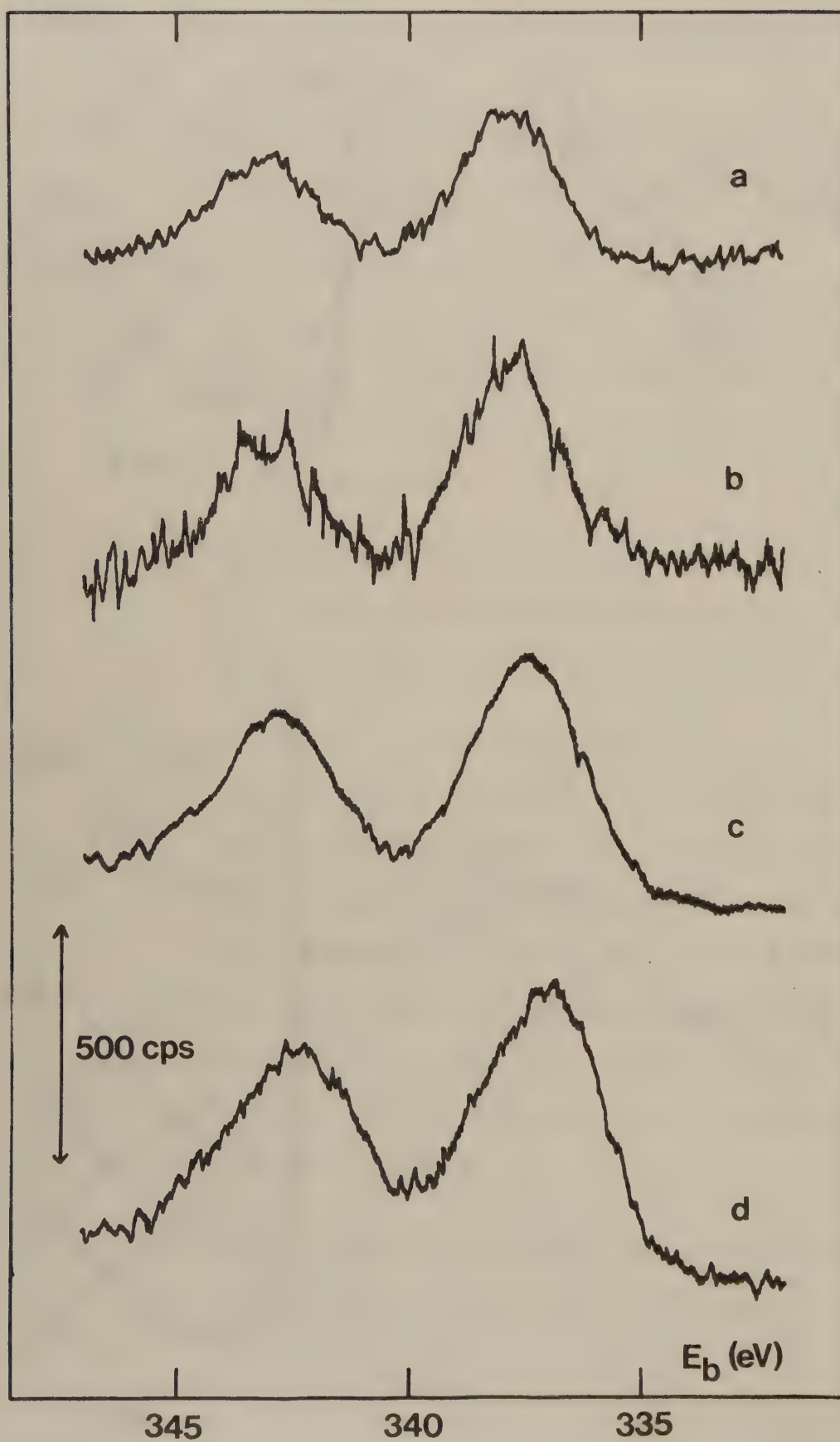


Fig 3

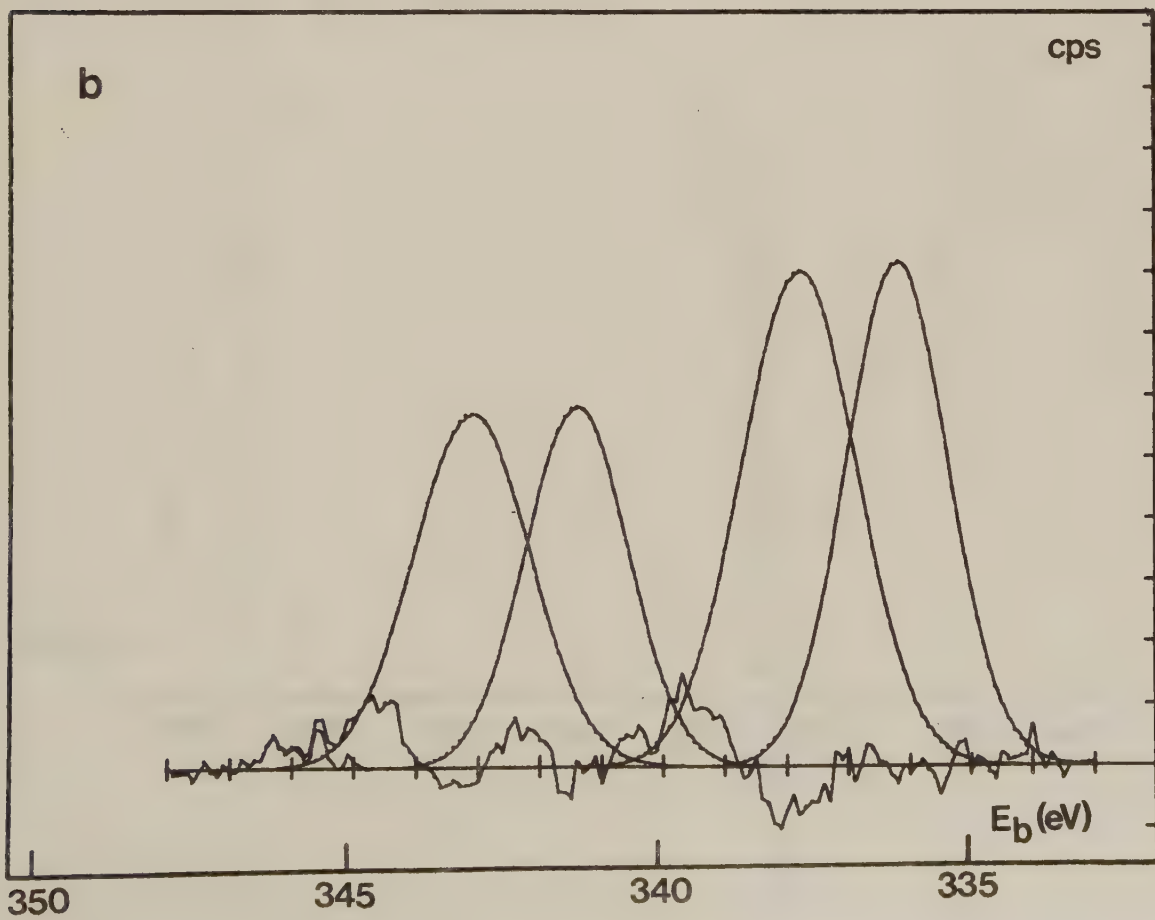
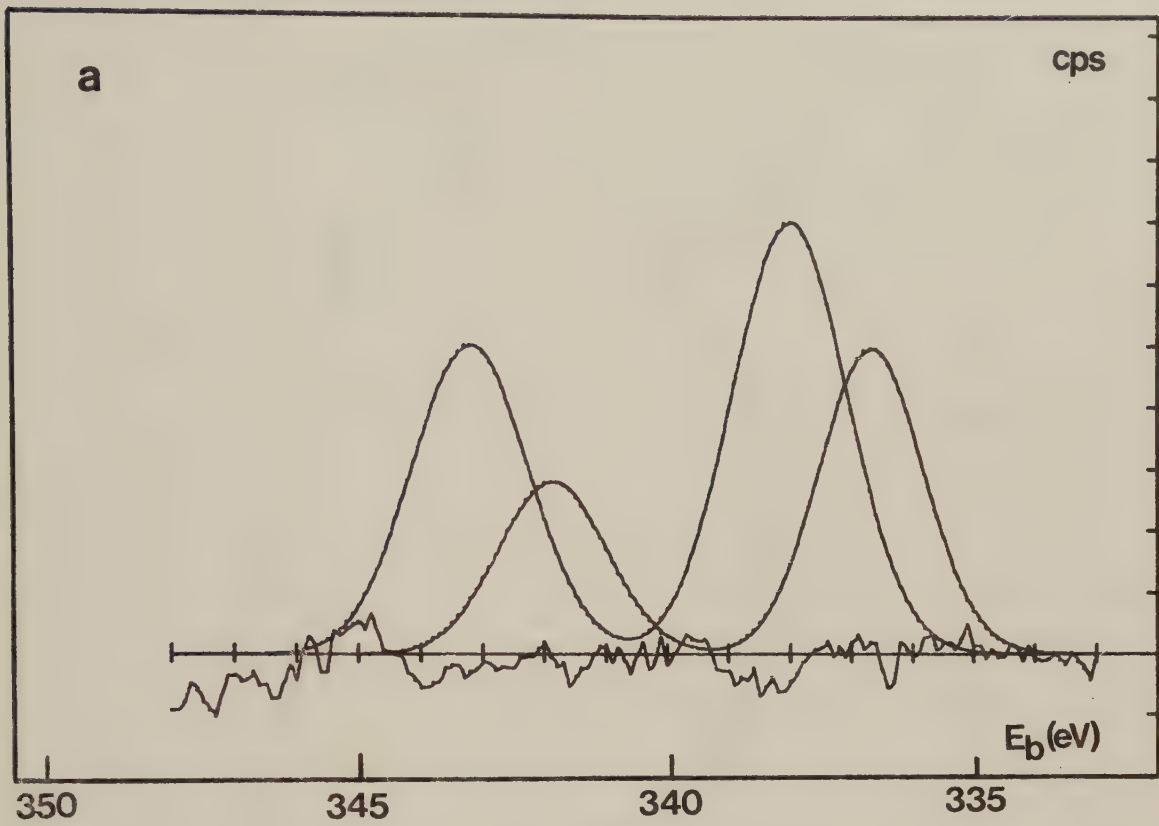


Fig 4

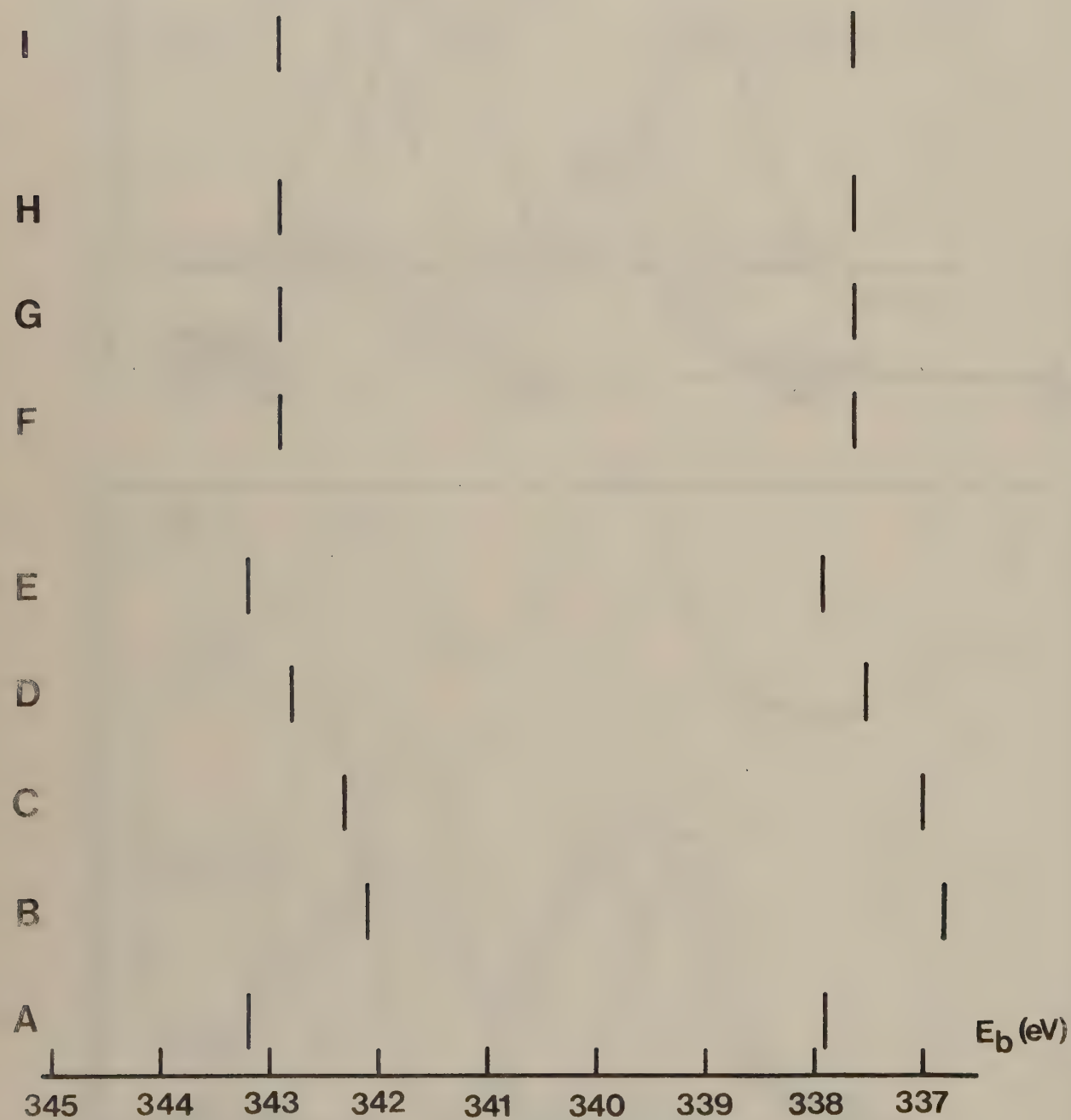
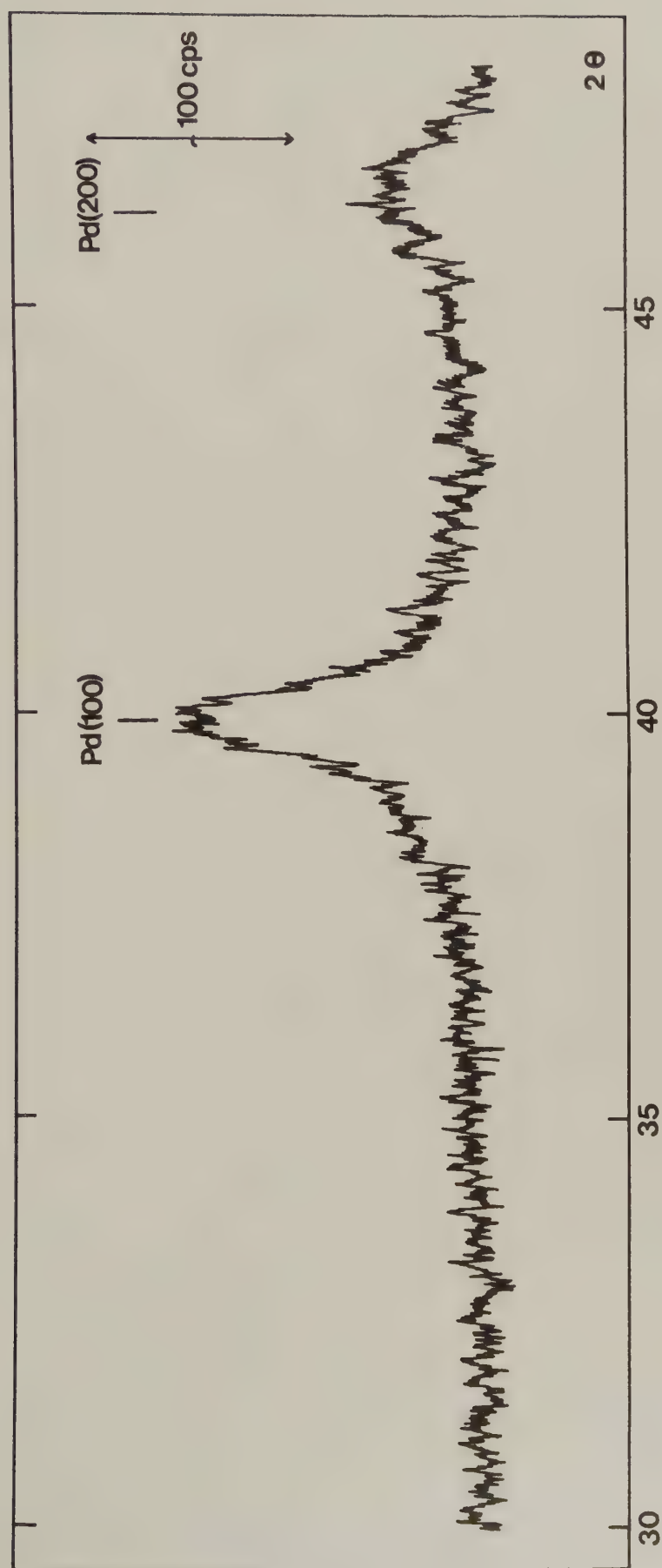


Fig 5







V



# ♣ Catalytic Hydrogenation of Soybean Oil with Rh(I) Dihydride Complexes As Catalysts

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## ABSTRACT

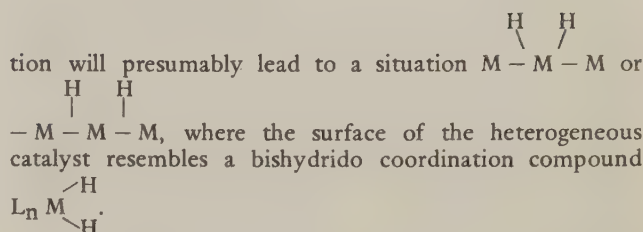
Cationic rhodium(I) complexes of the type  $[\text{NBD Rh L}_2]^+[\text{ClO}_4]^-$  (NBD = norbornadiene and L = diphenylphosphinoethane or triphenylphosphine) have been studied as catalysts for the hydrogenation of soybean oil. These catalysts give a good yield of products with *cis*-configuration. Indeed, hydrogenation could be performed under mild conditions (30 °C, 1 atm hydrogen pressure) to an iodine value of 80 with not more than 12% of *trans* monoenes and only 5% conjugated isomers formed. The results obtained are interpreted on the basis of the equilibrium  $\text{H}_2 \text{Rh L}_n^+ \rightleftharpoons \text{HRh L}_{n-1} + \text{H}^+$ . By the addition of acid ( $\text{HClO}_4$ ) the bishydrido form of the catalyst could be studied. With this system only small amounts of *trans* monoenes were formed and no other *trans* isomers could be detected. By the addition of a base such as triethylamine, the monohydridic form of the catalyst could be studied. In contrast to the bishydrido complex, this system gave large amounts of *trans* monoenes, together with *cis-trans* and *trans-trans* forms of the 18:2 acid. With both forms of the catalyst system, conjugated isomers were formed.

## INTRODUCTION

One consequence of interrupting the hydrogenation of vegetable oils before reaching completely saturated fatty acids is the formation of *trans* and other isomeric acids. In industrial operations these side reactions can in part be controlled and limited by reaction conditions such as temperature, pressure, agitating speed and the amount of catalyst (1). Certain additives can also be used to decrease the formation of *trans* acids (2). The recent discussion on the effects of *trans* acids on human health (3,4) has initiated a new interest in finding methods for producing hydrogenated fats with a low content of *trans* acids. To reach this goal, coordination catalysts seem useful, as one can influence their activity in various ways by changing their constitution. Nishiguchi and coworkers (5,6) have examined various transition metal complexes as catalysts for hydrogen transfer reactions from different hydrogen donors to olefinic bonds. Good results were achieved with  $\text{RuCl}_2(\text{PPh}_3)_3$  or  $\text{RuH}_2(\text{PPh}_3)_4$  with isopropanol as the hydrogen source. With indolene as hydrogen source, on the other hand,  $\text{PdCl}_2$  or  $(\text{NH}_4)_2\text{PdCl}_4$  proved to be the best catalysts.

Another type of coordination catalyst with unique *cis*-producing properties is arene chromium tricarbonyl. This catalyst has been investigated in great detail by Frankel et al. (7,8,9,10). A common feature of  $\text{RuH}_2(\text{PPh}_3)_4$  and arene chromium tricarbonyl is that in both cases a bishydrido complex,  $\text{MH}_2$ , takes part in the reaction. Fragale et al. (11) have used different Ir and Rh complexes as catalysts and tried to correlate the catalytic activity and selectivity to the number of phosphine ligands coordinated to the metal. They found that for Rh complexes the phosphine rich catalysts were highly active and produced the highest amount of *trans* isomers.  $\text{RhCl}(\text{PPh}_3)_3$  was an exception, as this complex produced the lowest *trans* content although it gave the highest hydrogenation rate.

It may be of some interest in this connection that in heterogeneous catalysis, changes in process variables that increase the hydrogen concentration decrease the formation of *trans* isomers (12). An increase in hydrogen concentra-



As a consequence of the above observations we started to study other coordination catalysts known to form dihydrides. An interesting example of such complexes is the cationic rhodium(I) complex  $\text{NBD Rh}^+(\text{phosphine})_2$ , where NBD = norbornadiene. This and similar complexes have been thoroughly investigated by Schrock and Osborn (13, 14,15) as hydrogenation catalysts for other substrates but not—to our knowledge—for fatty oils. Among the advantages of this system one can mention that the catalyst is active at low temperatures (30 °C) and low hydrogen pressure (1 atm). It is also possible to heterogenize this type of complex by incorporating the phosphine ligand into polymeric matrices, either organic, as polystyrene (16), or inorganic, as silica. As the complex is cationic it ought, in theory, to be possible to use ion exchangers like zeolites for the same purpose. The possibility of heterogenizing the catalyst is important for industrial applications of the catalyst.

Also from the viewpoint of basic research this rhodium complex is interesting. Schrock and Osborn (13) have established that the catalyst under hydrogen exists in an equilibrium between mono- and dihydridic species (Eq. [I]).



As can be seen from Eq. I, catalysis by both monohydrido and bishydrido complexes can be studied using the same metal and the same set of ligands only varying the pH. In this respect the system is rather unique (15).

This study was undertaken in order to gain some information on whether bishydrido complexes are important in the selective hydrogenation of polyunsaturated fats to *cis*-unsaturated products.

## EXPERIMENTAL PROCEDURE

### Chemicals

All solvents used were of analytical grade quality and used without further purification. Refined soybean oil was a gift from AB Karlshamns Oljefabriker, Karlshamn, and used as received.  $\text{Rh NBD Cl}_2$  was purchased (Strem Chemical);  $\text{Rh}(\text{NBD})\text{acac}$ ,  $[\text{Rh NBD}(\text{PPh}_3)_2]^+[\text{ClO}_4]^-$  and  $[\text{Rh NBD}(\text{diphos})]^+[\text{ClO}_4]^-$  were prepared according to reported methods (17). NBD = norbornadiene, acac = acetylacetonate, diphos =  $(\text{C}_6\text{H}_5)_2\text{P-CH}_2\text{-CH}_2\text{-P}(\text{C}_6\text{H}_5)_2$ . We have found that if oxidizing agents (peroxide in tetrahydrofuran [THF] or hydroperoxides in soybean oil) are present the catalyst will be easily oxidized and destroyed.



### Hydrogenations

The hydrogenation experiments were performed with the same type of apparatus and experimental procedure that was used in Ref. 13. For all the experiments, the results of which are given in the figures, we have used the following experimental conditions: temperature 32 C, total pressure 1 atm (no correction for vapor pressure of solvent was made), 1.0 ml soybean oil, acetone as solvent to a total volume of 10.0 ml, and catalyst concentration 7.2 mM. Perchloric acid  $\text{HClO}_4$  or triethylamine  $\text{NEt}_3$  was added as acetone solutions. The concentration of these additives are given in the figures. Samples were withdrawn and 1.0 ml n-hexane was added. These solutions were then passed through an  $\text{Al}_2\text{O}_3$ -column in order to remove the dissolved catalyst. The solvent was evaporated from the samples with nitrogen at room temperature. Methylations of the samples were done using sodium methoxide as catalyst.

### Analysis

The gas liquid chromatography (GLC) procedure was similar to that used earlier to separate *cis* and *trans* isomers (18,19): methylated samples were analyzed using an OV 275 (15% on P AW-DMCS 70/80) column (600 cm x 1/8 in.) (Chrompack, Holland). The column temperature was 210 C, and the injector and detector temperature was 250 C. The flow rate of the carrier gas, nitrogen, was 20 ml/min. The gas chromatograms were evaluated by a peak triangulation procedure.

To check the *trans* content derived at on GLC analysis, some selected samples were subjected to infrared analysis of the *trans*-content (20). As the method (20) is not applicable to samples containing large amounts of conjugated esters we have preferred to use the *trans*-values found by GLC analysis when presenting the results (Figs. 2-4 and Table I). Because of the small amount of oil in each sample, the procedure in Ref. 20 was not followed exactly. Instead of weighing the oil to be analyzed, we have measured the absorption intensity of the  $\text{C}=\text{O}$  stretching vibration to determine the amount of oil in the  $\text{CS}_2$ -solution. This method proved to give an accuracy reasonably comparable to that of the GLC analysis.

### RESULTS AND DISCUSSION

The first complex that we tested for the catalytic hydrogenation of soybean oil was the triphenylphosphine complex  $\text{NBD Rh}^+(\text{PPh}_3)_2\text{ClO}_4^-$ . The activity of this complex is very low. This observation stands in contrast to the findings of Fragale et al. (11), who used similar complexes, e.g.,  $\text{COD Rh}(\text{PPh}_3)_2^+ \text{BPh}_4^-$  (COD - cyclooctadiene), to catalyze the hydrogenation of soybean oil. The main difference between these two complexes is the anion, since neither COD nor NBD are present in the active species. Schrock and Osborn (17) have, however, pointed out that such complexes with the tetraphenylborate anion have a "complicated solution behavior." In acetone solution, they claim (17),  $\text{COD Rh}(\text{PPh}_3)_2^+ \text{BPh}_4^-$  is converted to the two species  $\text{Rh}(\text{COD})\text{BPh}_4$  and  $\text{Rh}(\text{PPh}_3)_2\text{BPh}_4$ , where one of the phenyl groups of the anion is coordinated to the metal atom via  $\pi$ -bonding. It is therefore not surprising that the  $\text{BPh}_4^-$  and  $\text{ClO}_4^-$  systems give different results.

We believe that the low rate we have found is caused by the formation of the complex  $\text{Rh}(\text{diene})_2\text{PPh}_3^+$ . This diolefin complex reacts presumably only very slowly with  $\text{H}_2$  or perhaps not at all. No attempts have been made, however, to isolate the diolefin complex or to identify it in solution by spectroscopic methods. The explanation sug-

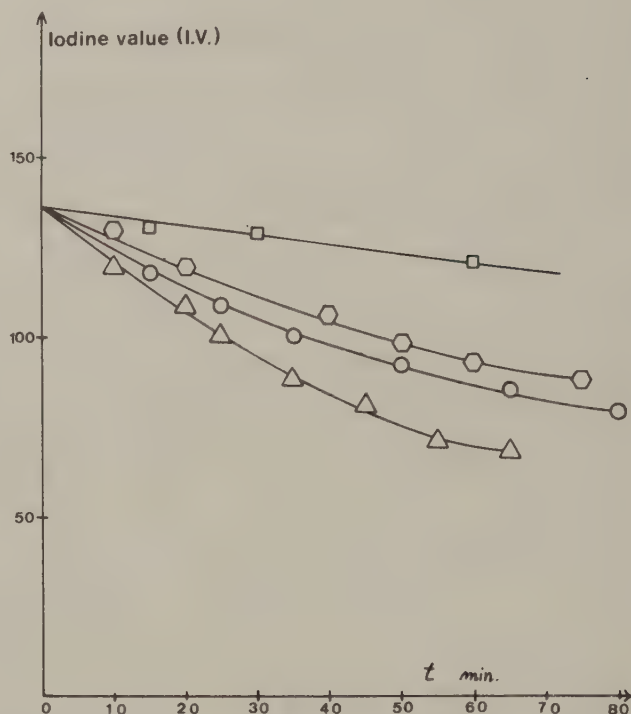


FIG. 1. Rate of reaction in hydrogenation of soybean oil (1.0 ml) catalyzed by NBD Rh diphos<sup>+</sup>  $\text{ClO}_4^-$  (7.2 mM) in acetone solution. Total volume 10.0 ml. Temperature 32.0 C. Key:  $\Delta$  = no additives;  $\circ$  =  $\text{NEt}_3$  added [ $\text{NEt}_3$ ] = 2 mM;  $\circ$  =  $\text{NEt}_3$  added [ $\text{NEt}_3$ ] = 10 mM;  $\square$  =  $\text{HClO}_4$  added [ $\text{HClO}_4$ ] = 21 mM.

gested above is put forward by analogy, as it is known from the work of Schrock and Osborn (15) that 1-3-butadiene reacts to form  $\text{Rh}(\text{diene})_2\text{PPh}_3^+$ , which adds hydrogen very slowly.

To prevent the formation of strong diolefin complexes Schrock and Osborn (15) have suggested the use of chelate forming ligands instead of monodentate ones. A drastic change in catalytic activity (about 10 times increase) was actually noted by us when  $[\text{NBD Rh diphos}]^+[\text{ClO}_4]^-$  was used instead of the triphenylphosphine complex. We have therefore concentrated our study on this complex.

In order to compare the effect on the product distribution of the action of mono- and bishydrido catalysts a series of hydrogenation experiments was done at varying acidity. Perchloric acid was used to shift the equilibrium (Eq. 1) towards the bishydrido side and triethylamine was used to shift it towards the monohydrido side. The results of these experiments are shown in Figures 1-4.

**Product distribution.** As stated in the introduction, the purpose of this study was to find out if the degree of formation of *trans*- and other isomers was dependent on the ratio between mono- and bishydrido catalysts. To discuss our results we refer to Figs. 2-4 and Table I. For the sake of clarity these figures have been divided into two parts. Part B represents the undesired products such as *trans* 18:1, nonconjugated *cis-trans* and *trans-trans* 18:2, and conjugated isomers. (In a separate test using a column separating conjugated from nonconjugated isomers but not differentiating *cis* and *trans*, we found one peak corresponding to 18:2 nonconjugated, the content of which was equal to the sum of the components designated as 18:2 *trans-trans*, 18:2 *cis-trans* and 18:2(*cis-cis*) in Fig. 4.) One notices that the product distribution curves for acid addition (Fig. 3) are about identical to those of the system with no additions (Fig. 2). This must mean that all rate parameters are

changed to about equal degree—even if they are much smaller for the acid addition case (Fig. 1). This in turn, must mean that the same active intermediate is operating in both cases but that its concentration for some reason is decreased when acid is added. (The reason for the decreased rate will be discussed together with the catalytic activity in the following section.)

This active intermediate is probably the diene complex "A" formed by coordination of linoleic acid to  $\text{Rh}^+$  diphos (Fig. 5). From this intermediate no dependence on acid addition would be expected. Such a dependence would be found, however, if either  $\text{H}_2\text{Rh}^+\text{diphos}$  or  $\text{HRh diphos}$  were the dominating species in solution. From A the reaction can proceed in two ways, either a reaction with  $\text{H}_2$  which leads to saturation of one of the double bonds, or conjugation via an allylic rearrangement of the  $\text{Rh}^+$  diene diphos complex prior to reaction with  $\text{H}_2$ . The concentration of conjugated isomers reaches a maximum of 16% at

an iodine value of 110, whereafter it decreases (Figs. 2 and 3). The presence of such relatively large amounts of conjugated isomers in the reaction mixture means probably that unconjugated diene can substitute the conjugated isomer bound in species B. This in its turn means that the complex binding ability of the nonconjugated isomer does not differ much from that of the conjugated isomer. In this respect the diene present in soybean oil behaves differently from what has been found for other nonconjugated dienes, e.g., 1,4-cyclohexadiene (15). The conjugated isomer formed from 1,4-cyclohexadiene is only liberated after reaction with either  $\text{H}_2$ , leading to the monomer, or a phosphin, which leads to substitution.

One notices further from Figures 2 and 3 that the concentration of *trans* 18:1 begins to rise when the concentration of the conjugated acids starts to decrease. This probably means that the *trans* 18:1 to the main part originates from the conjugated isomers, either *trans-cis* or *trans-trans*.

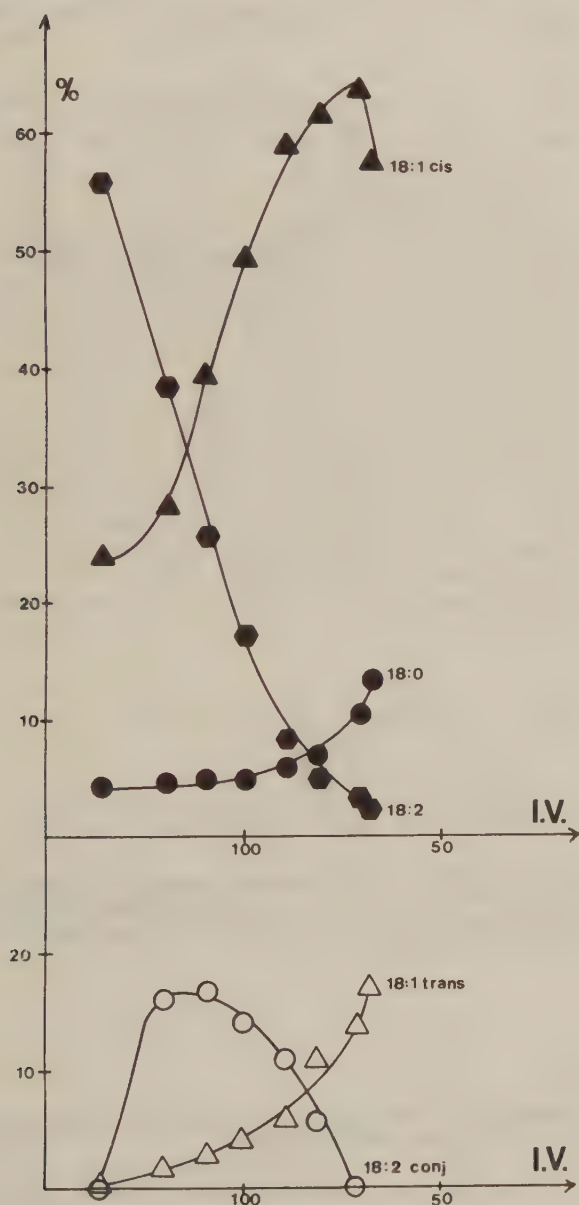


FIG. 2. Composition of the hydrogenated soybean oil at different iodine values. No additives. Conditions as in Figure 1. The 18:3 component in the starting mixture was converted so rapidly that it was not possible to detect.

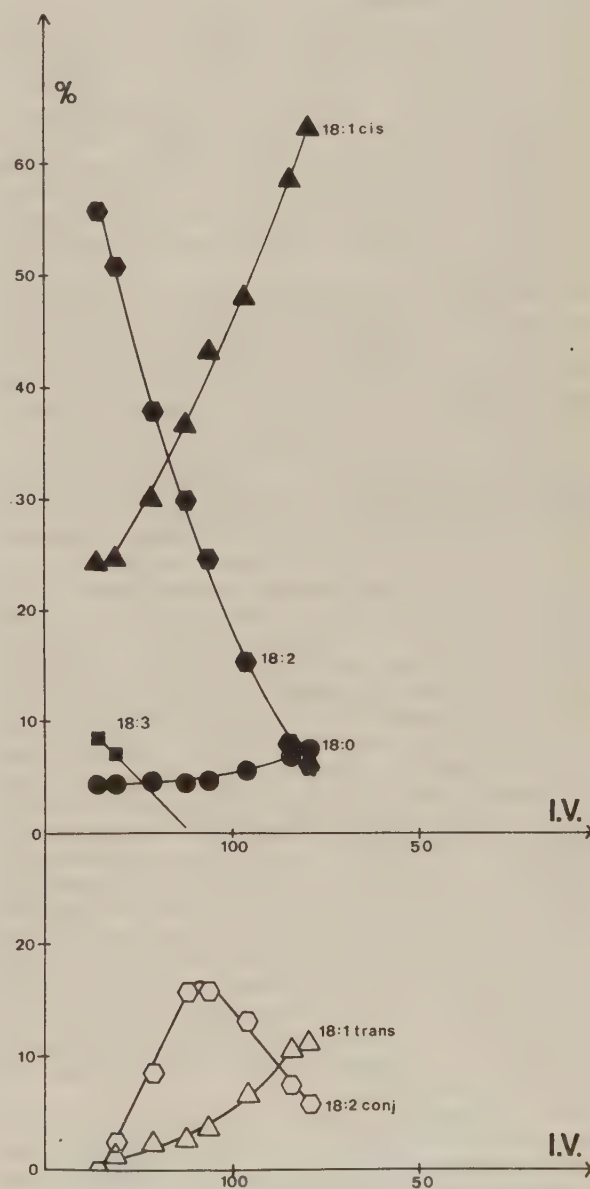


FIG. 3. Composition of the hydrogenated soybean oil at different iodine values ( $\text{HClO}_4$  added)  $[\text{HClO}_4] = 21 \text{ mM}$ . Conditions as in Figure 1.



From the simplified reaction scheme given in Figure 5 one can say that in order to avoid formation of conjugated isomers the rate of reaction with  $H_2$  ( $K_1$ ) must be much higher than the rate of conjugation ( $K_2$ ). This might be possible to achieve by using a bulky ligand which by steric influence makes the allylic rearrangement more difficult.

The reaction possibilities depicted in Figure 5 correspond to the path C described by Osborn et al. (15), i.e., olefin coordination before reaction with  $H_2$ . If, however, the equilibrium  $MH_2^+ \rightleftharpoons MH + H^+$  is shifted strongly towards the left side no further change in product distribution on addition of acid can be observed. Therefore, the presence of the dihydride route (path B) cannot be excluded.

In the scheme given by Schrock and Osborn the only way to convert the system to the monohydride is to shift the equilibrium  $M^+H_2 \rightleftharpoons MH + H^+$ . The drastic change of the product distribution pattern found upon adding the base to the solution (Fig. 4) indicates a conversion of the system to the monohydride. Thus, only small amounts of the dihydride exists in solution. The *trans* 18:1 acid reaches values close to 50% and the hydrogenation proceeds to the saturated acid 18:0. Also the formation of nonconjugated *cis-trans* 18:1 and *trans-trans* 18:2 can be noted. This pattern has all the characteristics of a single M-H attack on an isolated olefin bond. We suggest that the action of the base (triethylamine) is two-fold: (a) A shift of equilibrium 1 towards the right side to form the  $L_n RhH$  complex. (b) Blocking some of the coordination sites of the metal atom. This second effect will be discussed more when dealing with the catalytic activity.

**Catalytic activity.** The highest activity was obtained (Fig. 1) when the complex was used without additives. The addition of  $HClO_4$  to the system results in a lowering of the activity. Thus the addition of acid ( $HClO_4$ ) causes a decrease of the overall reaction rate but retains the product distribution pattern. This is in contrast to the reports of Osborn et al. (13). They found a distinct difference in the production of isomers parallel to that of the rate decrease on addition of  $HClO_4$ . This effect was found for monoenes, however, (13). For dienes no pronounced variation in either reaction rate or product pattern was found on acid addition (15). The decrease in rate of hydrogenation that we have found in this investigation (Fig. 1) is probably caused by a decrease in the concentration of species A (Fig. 5). Actually at higher acid concentration the rate is lowered even more. One way by which the concentration of species A can be decreased is by oxidation of Rh(I) to Rh(III). It is possible that the oxidizing acid ( $HClO_4$ ) could produce hydroperoxides or perhaps more likely epoxides from the unsaturated acids originally present in the soybean oil. These products can act as catalyst poisons or perhaps even oxidize Rh(I) to Rh(III) and destroy the active intermediate. This explanation is put forward on the basis of hydrogenation experiments done with oxidized oils: Oils with peroxide values of 4 were not hydrogenated with the present system.

Another possible explanation is the effect that arises from specific interaction of protons on the more or less negatively charged carbon atoms  $\pi$ -bonded to the transition metal atom. Hence—and because of the positive charge of this metal atom—repulsion takes place that decreases the stability of the species A.

Even the addition of  $NEt_3$  to the system caused a decreased activity, compared to the activity of the system without additives (Fig. 1). This can be explained if one takes into account that triethylamine is not only a Brønsted base that can shift the proton equilibrium (Eq. II), but also a Lewis base that can coordinate to the metal. By coordination of  $NEt_3$  to the metal (Eq. 3), coordination sites on the

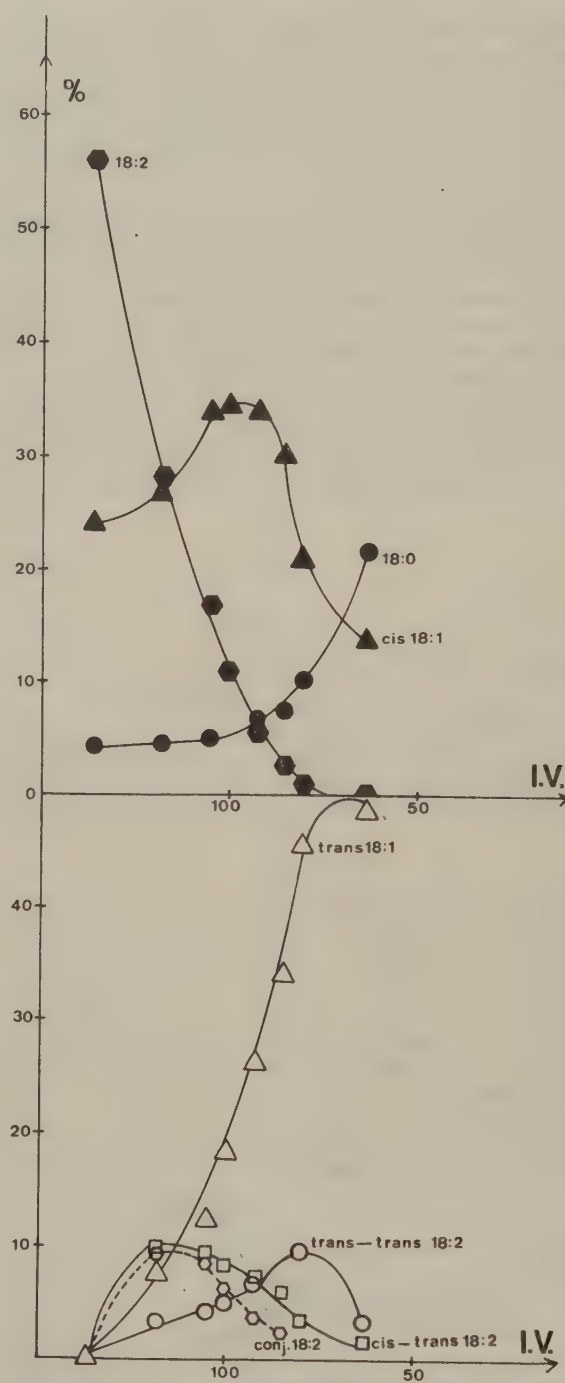


FIG. 4. Composition of the hydrogenated soybean oil at different iodine values  $NEt_3$  added.  $[NEt_3] = 2$  mM. Conditions as in Figure 1. As in the experiment with no additives it was not possible to detect the 18:3 component.

TABLE I

Composition of the Hydrogenated Oil at Some Selected Iodine Values. Data from the run without additives.

| I.V. | 18:0<br>% | <i>cis</i> 18:1<br>% | <i>trans</i> 18:1<br>% | <i>cis</i> 18:2<br>% | conj isomers<br>% |
|------|-----------|----------------------|------------------------|----------------------|-------------------|
| 100  | 4.8       | 48.2                 | 4.0                    | 16.8                 | 13.6              |
| 80   | 6.8       | 61.2                 | 10.4                   | 5.2                  | 4.8               |

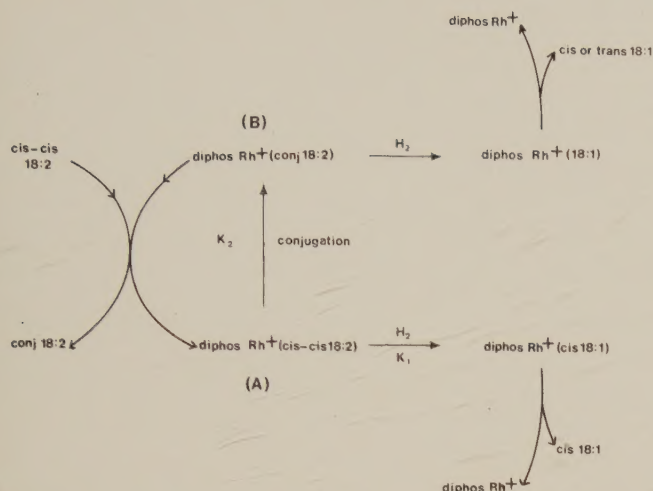
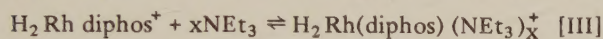
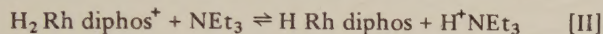


FIG. 5. Reaction scheme suggested for the hydrogenation of linoleic acid esters.

catalyst are blocked and the activity lowered:



The suggested explanation is supported by the following: If the concentration of added NEt<sub>3</sub> is reduced, and consequently less blocking of rhodium occurs, the catalytic activity as reported in Figure 1 is increased. The number of amine molecules that can add to the complex (i.e. *x* in Eq. III) is most probably greater than one. Therefore, it is quite reasonable that the blocking effect (Eq. III) of NEt<sub>3</sub> is more concentration-sensitive than the mere buffering action (Eq. II). Further support to this interpretation is the observation by Schrock and Osborn (13) that acetonitrile is not a suitable solvent because of the formation of a strong complex.  $\text{H}_2 \text{Rh(PPh}_3)_2 (\text{NC}\cdot\text{CH}_3)_2^+$ .

The model of hydrogenation suggested in the present paper conforms to our reported observations and to those of earlier investigators (13-15,17). In order to substantiate

the reasoning, further work should include spectroscopic studies on the interaction of protons with  $\pi$ -bonded metal-diene complexes and on how ligand basicity and ligand bulkiness influence the reaction. A study using nonoxidizing, noncoordinating acid, like HBF<sub>4</sub>, could also give valuable information.

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#### REFERENCES

1. Allen, R.R., and J.E. Covery, Jr., JAOCS 47:494 (1970).
2. Dutch Pat. Unilever N.V.P. appl. 7813005-1.
3. JAOCS 53:466A-468A Abstracts 146-164 (1976).
4. Squotas, D., and F.A. Kummerow, Am. J. Clin. Nutr. 23:111 (1970).
5. Nishiguchi, T., T. Tagawa, H. Imai and K. Fukuzumi, JAOCS 54:144 (1977).
6. Tagawa, T., T. Nishiguchi and K. Fukuzumi, Ibid. 55:332 (1978).
7. Frankel, E.N., and F.L. Little, Ibid. 46:256 (1969).
8. Frankel, E.N., and R.O. Butterfield, J. Org. Chem. 34:3030 (1969).
9. Frankel, E.N., JAOCS 47:11 (1970).
10. Awl, R.A., E.N. Frankel and J.P. Friedrich, Ibid. 55:577 (1978).
11. Fragale, C., M. Gargano, T. Gomes and M. Rossi, Ibid. 56:498 (1979).
12. Puri, P.S., Ibid. 55:865 (1978).
13. Schrock, R.R., and J.A. Osborn, J. Am. Chem. Soc. 98:2134 (1976).
14. Schrock, R.R., and J.A. Osborn, Ibid. 98:2143 (1976).
15. Schrock, R.R., and J.A. Osborn, Ibid. 98:4450 (1976).
16. Strukul, G., M. Bonivento, M. Graziani, E. Cernia and N. Palladino, Inorg. Chim. Acta 12:15 (1975).
17. Schrock, R.R., and J.A. Osborn, J. Am. Chem. Soc. 93:2397 (1971).
18. Smith, L.M., W.L. Dunkeley, A. Franke and T. Dairike, JAOCS 55:257 (1978).
19. Dittmar, K.E.J., H. Heckers and F.W. Melcher, Fette, Seifen Anstrichm. 80:297 (1978).
20. "Official and Tentative Methods of the American Oil Chemists' Society", Vols. 1&2, 3rd ed., 1973, AOCS, Champaign, IL, Method Cd 14-61.

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